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PB80-105166

Treatment of Organic Chemical Manufacturing Wastewater for Reuse

Union Carbide Corp, South Charleston, WV

Prepared for

Robert S Kerr Environmental Research Lab, Ada, OK

Aug 79

United States
Environmental Protection
Agency

Robert S. Kerr Environmental Research
Laboratory
Ada OK 74820

EPA-600/2-79-184
August 1979

PB80-105166

Research and Development

EPA

Treatment of Organic Chemical Manufacturing Wastewater for Reuse

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TECHNICAL REPORT DATA

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1. REPORT NO. EPA-600/2-79-184	2.	3. RECIPIENT'S ACCESSION NO. PB80-105166
4. TITLE AND SUBTITLE Treatment of Organic Chemical Manufacturing Wastewater for Reuse		5. REPORT DATE August 1979 issuing date 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Michael Scherm, Patrick M. Thomasson, Lester C. Boone, Lawrence S. Magelssen		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Union Carbide Corporation Chemicals and Plastics Division, R&D Box 8361, Technical Center South Charleston, West Virginia 25303		10. PROGRAM ELEMENT NO. 1BB610 11. CONTRACT/GRANT NO. S801398
12. SPONSORING AGENCY NAME AND ADDRESS Robert S. Kerr Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Ada, Oklahoma 74820		13. TYPE OF REPORT AND PERIOD COVERED FINAL 4/76 to 12/76 14. SPONSORING AGENCY CODE EPA/600/15

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This research demonstrated the quality of water produced by each step of a state-of-the-art, commercially available process sequence and determined the feasibility and economics of renovating organic chemical wastewater for reuse as boiler feedwater or cycle cooling water. The 5-gpm pilot facility, located in Puerto Rico in the organic chemical manufacturing plant of Union Carbide Caribe Inc., consisted of sedimentation/filtration, carbon adsorption, pressure filtration, reverse osmosis, and ion-exchange. A pilot-scale boiler tested the product water as boiler feedwater at pressures, temperatures, and heat fluxes typical of full-scale manufacturing facilities. A pilot-scale cooling tower and heat exchangers determined feasibility as cycle cooling water makeup and chemical treatment requirements for makeup waters of varying quality from different points in the treatment sequence. The pilot boiler operated successfully at 180,000 BTU/ft^2-hr, 1500 psig, and 750°F superheat temperature with renovated wastewater. The cooling water test-loop studies indicated that special metallurgy would be required for the use of this renovated wastewater for cooling water. The total annualized cost of wastewater renovation to boiler feedwater quality at 67 percent water recovery, not including the cost of sludge or brine disposal, was $7.50/1000 gallons of product water in 1978.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Activated Sludge Process Activated Carbon Treatment Osmosis Ion Exchangers Filtration Petrochemistry Cooling Water	Recycle Reuse Boiler Water	68D

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 173
	20. SECURITY CLASS (This page) Unclassified	22. PRICE A08- A01

*U.S. GOVERNMENT PRINTING OFFICE:1979-657-060-5372

EPA-600/2-79-184
August 1979

TREATMENT OF ORGANIC CHEMICAL MANUFACTURING WASTEWATER FOR REUSE

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to the knowledge essential if the EPA is to meet the requirements of environmental laws that it establish and enforce pollution control standards which are reasonable, cost effective and provide adequate protection for the American public.

William C. Galegar

W. C. Galegar
Director
Robert S. Kerr Environmental Research Laboratory

ABSTRACT

This research program was initiated with the overall objectives of demonstrating the quality of water produced after each step in the treatment of the raw wastewater of an organic chemical plant from a best state-of-the-art commercially available process sequence, and determining the feasibility and economics of renovating this organic chemical wastewater for reuse as boiler feedwater or cycle cooling water.

A pilot facility was designed and constructed to renovate 5 gallons per minute (gpm) of biological effluent from the Union Carbide Caribe Incorporated (UCCI) organic chemical manufacturing plant in Puerto Rico, through best state-of-the-art, commercially available processes for the removal of suspended solids, residual organics and dissolved salts. The process sequence consisted of sedimentation/mixed-media filtration, carbon adsorption, pressure filtration, reverse osmosis, and ion-exchange and was followed by a pilot-scale boiler designed to test the reusability of the renovated wastewater as boiler feedwater at pressures, temperatures and heat fluxes typical of full-scale manufacturing facilities. A pilot-scale cooling tower and heat exchangers were designed and operated to determine chemical treatment requirements for makeup waters of varying quality taken from different points in the treatment sequence.

After eight months of continuous operation, the renovation sequence was evaluated in terms of reduction efficiency across each process step. A maximum 67 percent water recovery was achieved. From these pilot data, full-scale renovation facilities were designed and costs were estimated for a similar sequence treating 1500 gpm and 3000 gpm. Based upon a ±25 percent estimate, not including the cost of sludge or brine disposal, the total annualized cost of wastewater renovation to boiler feedwater quality at 67 percent water recovery was estimated to be \$2.00/cubic meter (m^3) (\$7.50/1000 gallons (gal)) product water in 1978.

The pilot boiler operated successfully at 180,000 BTU/square foot-hour (ft^2-hr), 1500 psig, and 750°F superheat temperature with renovated wastewater when compared to operation with the demineralized well-water presently used for feed to the full-scale plant boilers. The steam condensate derived from renovated wastewater was alightly more corrosive than that derived from the use of demineralized well-water as boiler feedwater.

The cooling water test loop, during 30-day test runs, utilized reverse osmosis permeate, activated carbon effluent, sedimentation/filtration effluent, and clarified biological effluent as makeup. Corrosion and heat transfer characteristics with these makeup waters were found satisfactory only with A-249 stainless steel, indicating that special metallurgy would be required for the use of this renovated wastewater for cooling water.

This report was submitted in fulfillment of Grant No. S-801398 by Union Carbide Corporation under the partial sponsorship of the U.S. Environmental Protection Agency. This report covers a period from April 1, 1976, to December 1, 1976; work was completed on December 1, 1976.

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ABBREVIATIONS

BFW -- boiler feedwater
BOD -- biochemical oxygen demand
BTU -- British thermal unit
BV/hr. -- bed volumes per hour
°C -- degree Centigrade
CA -- cellulose acetate
CE -- Combustion Engineering
cm -- centimeter
COD -- chemical oxygen demand
DWW -- demineralized well-water
°F -- degree Fahrenheit
ft. -- feet
F/M -- food to microorganism ratio
gm. -- gram
gpd -- gallons per day
gpm -- gallons per minute
in. -- inches
IWT -- Illinois Water Treatment Co.
Kg -- kilogram
Kwh -- kilowatt hour
l -- liter
lbs. -- pounds
lpm -- liters per minute
m -- meter
mg/l -- milligrams per liter
min. -- minutes
MLSS -- mixed liquor suspended solids
MLVSS -- mixed liquor volatile suspended solids
PA -- polyamide
psig -- pounds per square inch gage
PVC -- polyvinyl chloride
RO -- reverse osmosis
RSS -- recycle suspended solids
RWW -- renovated wastewater
SS -- suspended solids
SQ. FT. -- square feet
TOC -- total organic carbon
UCCI -- Union Carbide Caribe, Inc.
µl -- microliter
µmho -- micromho
UOP -- Universal Oil Products

ACKNOWLEDGMENTS

The following Union Carbide personnel contributed significantly to the conception, planning, and implementation of the experimental program: B. J. Brymer, J. A. Fisher, O. D. O'Bryan, C. T. Lawson, R. Ocejo, M. Ramos, R. C. Vaseleski, V. Vega. J. C. Boesch, W. Goff, J. Myers, and G. M. Whipple assisted in the full-scale design and cost analysis.

The design and cost estimates for full-scale reverse osmosis systems were prepared by M. Juar and T. Smith of Universal Oil Products (UOP).

The contributions of Mr. J. Shook et al., of Betz Environmental Engineers (BEE) in the design, implementation, and data evaluation of the pilot boiler tests are gratefully acknowledged.

The authors thank Dr. P. E. Des Rosiers, Staff Engineer, Mr. Leon Myers, Research Chemist, and Dr. T. E. Short, Project Officer, of the Environmental Protection Agency, who contributed to the planning of this joint research program.

SECTION 1

INTRODUCTION

Effective conservation of our natural water resources is high on the list of national objectives. Toward these objectives, increasingly stringent wastewater effluent standards, have recently been imposed. Indeed, the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500) have set a goal of zero discharge of pollutants into any navigable water by 1985. The implementation of a zero discharge goal would make wastewater reuse mandatory in the very near future. Unfortunately, existing secondary wastewater treatment facilities in the organic chemicals manufacturing industry are, in general, of the biological type which produce effluents not meeting the water quality criteria required of makeup water for most heat exchange systems; nor is the product suitable feed for typical water treatment facilities. This project was directed at investigating the current technology existing in the best state-of-the-art commercially available processes when applied toward the practical achievement of zero discharge through recycle of product for boiler feed or recycle cooling water makeup. The concept of zero discharge of treatment residues was not within the project scope.

Little information is available in industrial wastewater treatment literature pertaining to the reuse of renovated wastewater from large, multi-product organic chemical plants. Specifically, there are no references to a process sequence of commercially available technology to produce makeup for high temperature heat transfer systems or similar high-quality water. The Environmental Protection Agency's interest in developing general information which defines the acceptable limits for pollutants in reclaimed petrochemical wastewater when used as cooling tower or boiler makeup, coupled with Union Carbide's additional interest in wastewater recovery as a supplemental source of raw water led to this jointly funded large-scale pilot plant.

The pilot plant was designed and constructed to attain a high rate of water recovery while continuously processing the secondary effluent from a large organic chemical manufacturing complex. The sequence of processing steps which had the highest potential of producing high-quality boiler feedwater was selected from commercially available technology. Reuse feasibility was demonstrated in two carefully modeled heat transfer test loops. The cycle cooling water test loop was designed to provide heat transfer fouling rates, to define effective chemical treatment programs, and to evaluate the corrosion resistance of the three most common metals of construction for heat exchangers. Makeup water for the cooling tower from several sources within the treatment process was evaluated. The boiler test loop, which includes all of the appurtenances common to large, fairly sophisticated boilers, was capable of providing all of the performance data for steam generation over a wide range of pressure, temperature, and heat flux.

The pilot program's primary objective was to demonstrate the quality of water each step of the treatment can be expected to produce from an organic chemical plant's secondary wastewater treatment system and to determine the operating cost when this water is renovated for reuse as boiler feedwater or cycle cooling water makeup.

The wastewater reuse pilot plant was installed in Union Carbide Caribe, Inc.'s organic chemical manufacturing plant near Ponce, Puerto Rico, at a cost of $925,000. The experimental program extended over an eight-month period (April 1976 through November 1976) and incurred an operating cost of $800,000.

SECTION 2

CONCLUSIONS

The total annualized cost of producing water of boiler feedwater quality through a renovation sequence consisting of reactor clarifiers, carbon adsorption, pressure filtration, reverse osmosis and ion-exchange would be approximately \$2.00/m^3 (\$7.50/1,000 gal) in 1978, not including primary or secondary treatment costs or facilities for the handling and disposal of waste brines and sludges.

Carbon adsorption, including regeneration facilities, make up approximately 35 percent of the total fixed investment and greater than 30 percent of the total annual operating expenses.

Reverse osmosis facilities account for approximately 25 percent of the total fixed investment and 30 percent of the annual operating expense.

Waters of lesser quality than boiler feedwater could be obtained at significantly reduced costs for use in low pressure steam systems or as cooling water.

Any impurities that passed through the wastewater renovation sequence did not noticeably affect boiler deposition.

The amount of waterside deposit within the boiler when using renovated wastewater was less than that produced using plant boiler feedwater (demineralized well-water).

The quality of steam produced from the renovated wastewater was equivalent to that generated from demineralized well-water.

Superheater deposition using renovated wastewater was equivalent to that produced using demineralized well-water.

Condensate derived from using renovated wastewater as boiler feedwater appeared slightly more corrosive than condensate derived from demineralized well-water.

When renovated wastewater was used as cycle cooling water makeup, chromate treatment was effective in controlling the corrosion of A-214 carbon steel; however, unacceptable heat transfer characteristics resulted from the formation of scale.

The use of Zn/PO_4 corrosion inhibitor resulted in satisfactory heat transfer on carbon steel, but excessive corrosion was observed.

Only A-249 stainless steel was effective in maintaining satisfactory corrosion and heat transfer characteristics with the makeup waters and treatments tested. Special metallurgy would be required for the use of this renovated wastewater as cooling water.

SECTION 3

RECOMMENDATIONS

A high quality secondary effluent is necessary for effective operation of the tertiary wastewater renovation facilities. Since most secondary effluents in the organic chemicals industry are of the biological type with residual organics and solids, it is strongly recommended that every attempt be made to optimize the biological system prior to attempting wastewater renovation for reuse.

Only virgin activated carbon was used in the residual-organic adsorption step of these wastewater renovation process studies. Further adsorption tests with regenerated carbon are recommended before a final judgment is made on the efficacy and economics of this step of the renovation sequence.

The use of renovated wastewater as cycle cooling water should be considered in water-short areas, provided existing materials of construction in the heat exchange system are compatible or can be made compatible with the water. Stainless steel, or similar alloys, were recommended in the present case when the degree of renovation, beyond conventional biological treatment, involved only the removal of suspended solids and the addition of appropriate inhibitors and dispersants to the cycle water. More extensive renovation may make admiralty brass an acceptable construction material in some cases.

Because of the cost of renovation, the reuse of wastewater for high pressure boiler feedwater, while technically feasible, is not generally recommended. In cases where lesser qualities of water are acceptable for the production of low pressure steam, and the cost of the renovation sequence can be reduced, the reuse of wastewater for boiler feedwater is a viable alternative and is worthy of consideration.

SECTION 4

WASTEWATER RENOVATION FACILITIES

FACILITIES DESCRIPTION

The pilot treatment facilities, designed to operate continuously, included an activated sludge unit; a physical-chemical treatment system consisting of a suspended solids removal unit, an activated carbon unit, and a multi-media filtration unit; a demineralization system consisting of a reverse osmosis unit and primary and secondary deionization units; and a system for the collection and handling of waste sludge and backwash water for maximum water recovery. The process sequences selected were determined by bench-scale studies and literature survey as having the highest potential for producing boiler feedwater quality water from an organic chemical plant's process wastewater. The processes tested were considered the best state-of-the-art commercially available. Process design was done by Union Carbide Corporation's Environmental Engineering Group, with detailed design assistance from The Austin Company.

Many of the treatment steps incorporated into the pilot plant renovation processes were accomplished in commercially-available package units. The package units set the design flow rates throughout the treatment steps which were, consequently, greater than the test loop requirements. Cooling water test loop and boiler test loop makeup-water requirements were approximately 4.78 liters/minute (lpm) (1 gpm) and 1.89 lpm (0.5 gpm) respectively. The package units utilized were preassembled and included the sedimentation/filtration unit; the multi-media filter unit; the reverse osmosis unit; and the ion-exchange unit.

The pilot facilities were designed to operate continuously on the raw wastewater from Union Carbide Caribe's manufacturing units after primary clarification, pH adjustment, nutrient addition and equalization. For those units requiring backwashing or regeneration, intermediate storage capacity was provided to accumulate effluents from these units. These water inventories were arranged to provide backwashing, rinsing, and regenerant dilution water for each respective unit, as well as to provide an uninterrupted feed supply to the subsequent units and test loops.

The pilot plant process sequence is illustrated in the attached block flow diagram (Figure 1) and a photograph of a portion of the pilot facilities shown in Figure 2.

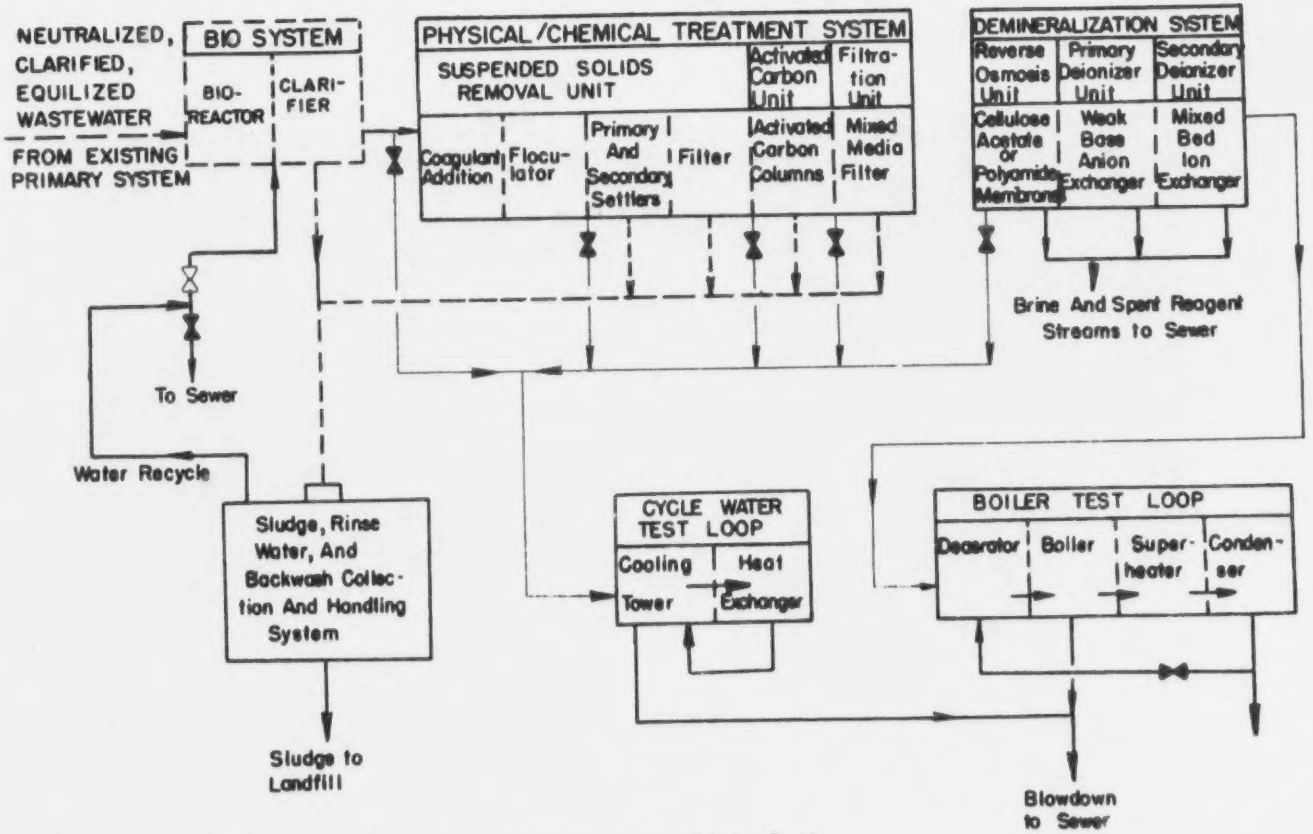
NEUTRALIZED, CLARIFIED, EQUILIZED WASTEWATER
FROM EXISTING PRIMARY SYSTEM
BIO SYSTEM
BIO-REACTOR
CLARI-FIER
PHYSICAL/CHEMICAL TREATMENT SYSTEM
SUSPENDED SOLIDS REMOVAL UNIT
Coagulant Addition
Flocu-lator
Primary And Secondary Settlers
Filter
Activated Carbon Unit
Activated Carbon Columns
Filtra-tion Unit
Mixed Media Filter
DEMINERALIZATION SYSTEM
Reverse Osmosis Unit
Cellulose Acetate or Polyamide Membrane
Primary Deionizer Unit
Weak Base Anion Exchanger
Secondary Deionizer Unit
Mixed Bed Ion Exchanger
Brine And Spent Reagent Streams to Sewer
To Sewer
Water Recycle
Sludge, Rinse Water, And Backwash Collection And Handling System
Sludge to Landfill
CYCLE WATER TEST LOOP
Cooling Tower
Heat Exchanger
BOILER TEST LOOP
Deaerator
Boiler
Super-heater
Conden-ser
Blowdown to Sewer

Figure 1. Block flow diagram for wastewater reuse pilot plant.

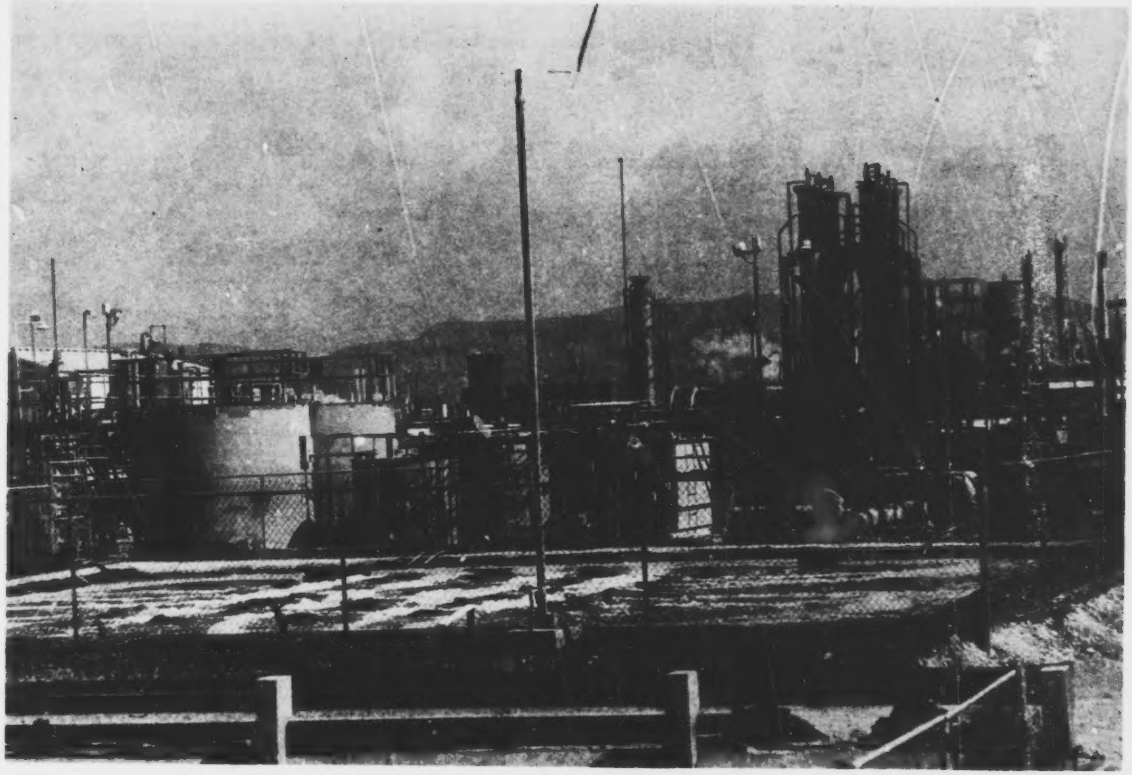

Figure 2. Pilot-plant wastewater renovation facilities showing activated sludge in foreground and tertiary facilities in background

Biological Treatment System

Biological treatment consisted of a very conservatively designed activated-sludge process comprised of a bioreactor, aeration equipment, and a clarifier (Figure 2). The equipment was sized for 7.5-day detention time, an influent of 28.4 lpm (7.5 gpm) (11,000 gpd (gallons per day)) of process wastewater, and a mixed liquor volatile suspended solids (MLVSS) concentration of 2,500 milligrams per liter (mg/l).

The bio-treatment system consists of a plastic lined earthen bioreactor and a 3.66-meter (m) (12-ft) diameter clarifier. Air was diffused into the bottom of the bioreactor through headers located under static mixers (POLCON) which provided mixing and distributed oxygen for support of the biological activity. Between the bioreactor and the clarifier, wastewater flowed through a level controlled weir box which maintained a constant flow to an agitated vessel wherein coagulants could be added to enhance settling of the biosolids. Sludge was recycled to the bioreactor at a rate necessary to maintain the proper MLVSS concentration and sludge age. Sludge wastage was measured daily by wasting into a waste sludge receiving tank before discharge to the waste sludge and backwash handling system. The clarified liquor flowed through an intermediate tank into the physical-chemical treatment system.

Physical-Chemical Treatment System

The physical-chemical treatment system consisted of a suspended solids removal unit, an activated-carbon adsorption unit, and a multi-media filtration unit. The influent to the physical-chemical treatment system was 18.9 to 26.5 lpm (5.0 to 7.0 gpm).

Sedimentation/Filtration--

The sedimentation/filtration unit removed suspended solids by coagulation, sedimentation, and filtration.

This unit was a packaged commercial unit (Neptune Microfloc) (Figure 3) consisting of an influent flow-splitting box, a rapid mix tank, a slow-mixed flocculator tank, primary and secondary tubular settlers, a mixed-media filter, a backwash water storage tank, and four chemical feed tank assemblies complete with mixers and metering pumps. Coagulating chemicals could be metered into the rapid-mix tank along with a controlled flow of clarified bio-effluent from the flow-splitter box. The effluent from the flocculator flowed over a weir into the first-stage tube settler, which contained settling tubes 5.08 centimeters (cm) (2 inches (in)) in depth and 26.54 cm (24 in) in length. The settling tubes were inclined at 60°. The settling tubes maintained a sludge blanket which promoted coagulation and provided a source of sludge for recycle to the rapid mix tank. Effluent from the first stage flowed into the second-stage settling chamber for

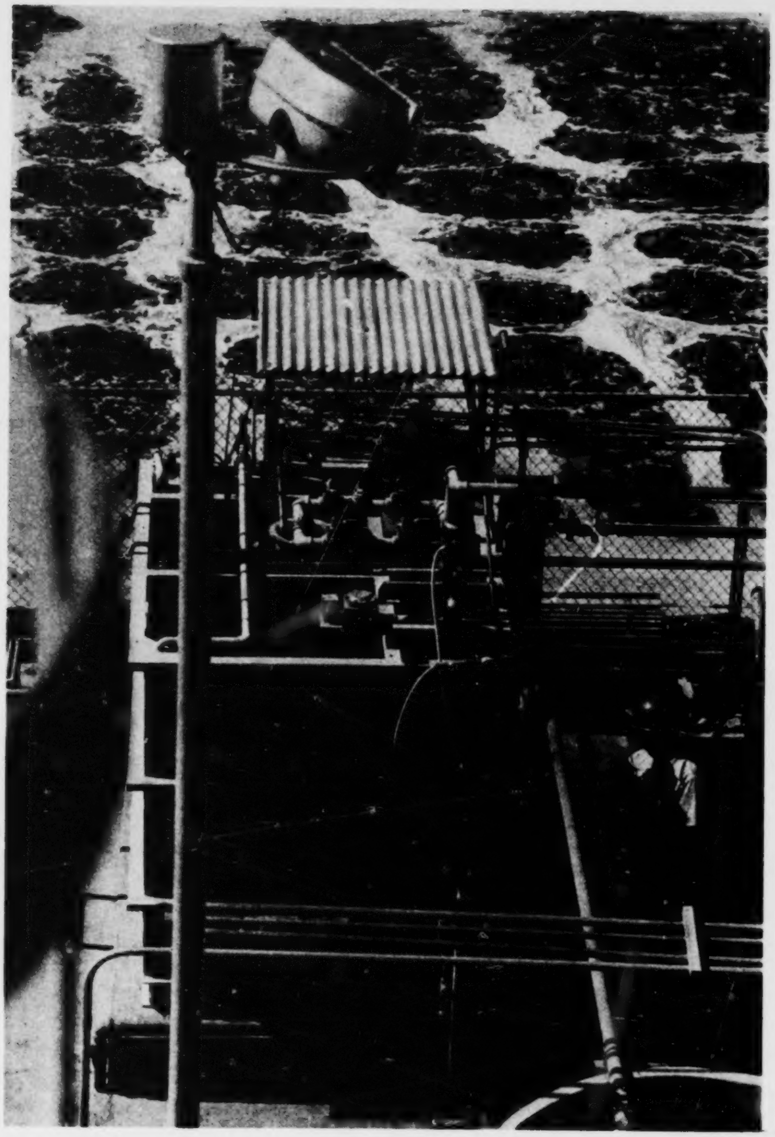

Figure 3. Sedimentation/filtration unit.

final clarification. This chamber contained modules composed of settling tubes 2.54 cm (1 in) in depth by 99.06 cm (39 in) in length, inclined slightly to facilitate drainage of the sludge during the backwash cycle. The second-stage tube settler effluent flowed by gravity into the mixed-media filter which removed most of the remaining suspended solids.

The filter and second-stage settlers were backwashed, manually or automatically, based on filter head loss. The backwash water with the accumulated solids and the wasted sludge from the first-stage settler was pumped to the waste collection tank in the waste sludge and backwash handling system.

Activated Carbon Adsorption Unit--

Effluent from the sedimentation/filtration unit flowed into the carbon adsorption system, which consisted of six 40-cm (16-in) diameter columns which were 7.6 m (25 ft) high and which had a 4.9-m (16-ft) bed depth (Figure 4). Initial testing of various combinations of parallel and series flow revealed that the best arrangement was a three beds-in-series in an expanded upflow mode. This arrangement allowed near maximum organic (COD) adsorption. The three carbon columns in series had an accumulated bed depth of 14.6 m (48 ft) which when operated at 18.9 lpm (5 gpm) throughput corresponds to a hydraulic loading of 159 lpm/m^2 (3.9 gpm/ft^2) and a total contact time of 0.59 Bed Volumes (BV)/hour (100 minutes).

All column charges were made using virgin granular carbon--Calgon Filtrasorb 300.

Multi-Media Filtration Unit--

A commercial multi-media filter unit, purchased from Illinois Water Treatment Co. (IWT), was used to remove any carbon fines from the activated carbon adsorption unit effluent (Figure 5). This unit, which operated at about 10 psig, consisted of 35.6-cm (14-in) diameter by 76.2-cm (30-in) deep bed composed of layers of coal, sand, and garnet. After filtration, the carbon column effluent entered the adsorber effluent tank which acted as a surge tank to provide an uninterrupted feed flow to the demineralization unit as well as backwash water for the activated carbon beds and the multi-media filter. Spent backwash water was routed to the waste sludge and backwash collection tank.

Demineralization System

The demineralization treatment system was designed to remove soluble compounds from the wastewater and consisted of a reverse osmosis unit, a primary deionizer unit, and a secondary deionizer unit.

Reverse Osmosis Unit--

The reverse osmosis (RO) unit, purchased from Universal Oil Products, was designed to operate automatically in a batch mode

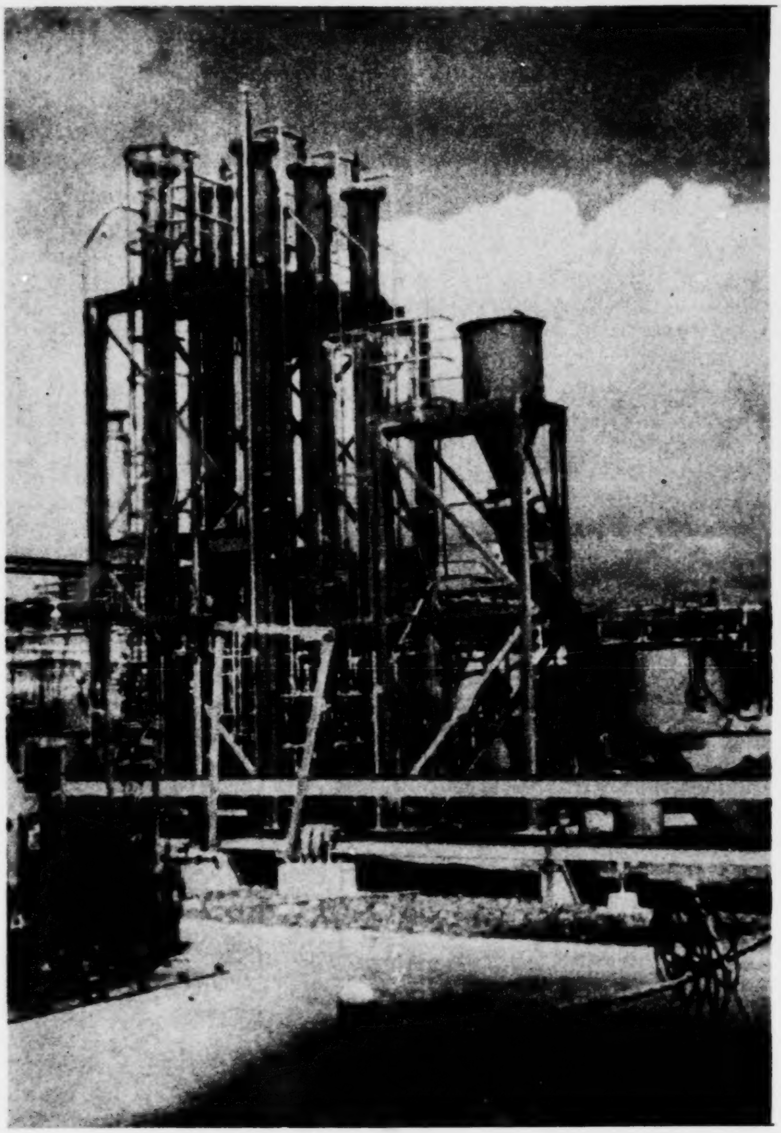

Figure 4. Activated carbon columns.

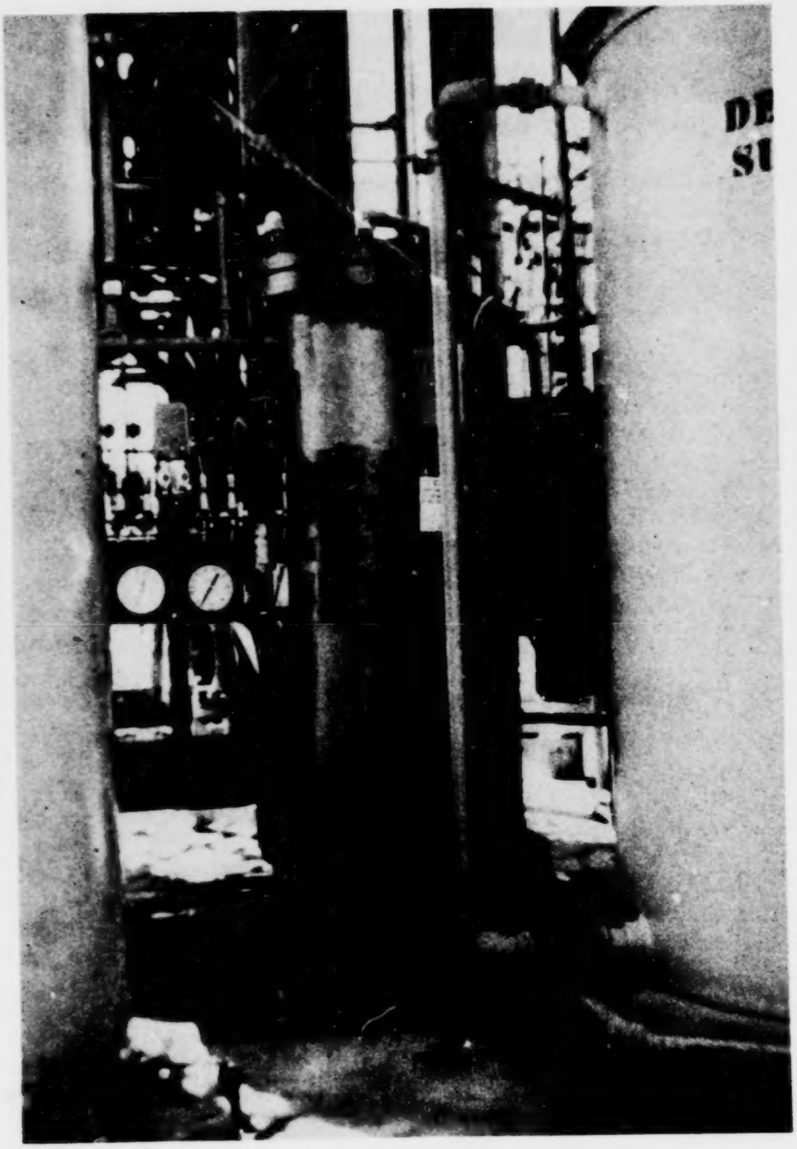

Figure 5. Multi-media filter.

and was intended to demineralize up to 90 percent of the influent water (Figure 6). The unit was also designed to accommodate modules of hollow fiber, spiral wound or tubular membrane configurations. The RO service pump transferred the filtered water from the demineralization supply tank into the two-compartment RO feed tank, from which a suction booster pumped the water through a 10-micron cartridge filter into the suction of the RO cycle pump. This suction booster-filter step insured an adequate water supply to the RO feed pump, thus preventing pump cavitation, plus it protected the membranes from most solids that passed through the multi-media filter. The RO system was equipped with in-line acid addition, and pH, flow, temperature, and permeate conductivity monitors. Automatic alarm and shutdown were provided for low flow, high temperature, high pH, and high permeate conductivity.

Tubular and spiral wound modules were used during the test period.

Tubular membrane configuration--The UOP OSMOTIK module utilized a filament-wound fiberglass tube, each tube containing an integrally formed 520 type cellulose acetate membrane on the inner surface. The 18-tube module had a membrane surface of 16.7 ft^2. These tubes, which were each 88 in in length, were contained within a hexagonal shroud or module, and were arranged for series flow by means of molded heads. A rod was positioned axially through each module to hold the assembly in place. A volume displacement rod was installed in each tube to reduce solids deposition and fouling of the membrane surface. The membrane unit consisted of one stage of 52 modules arranged in 13 parallel rows of 4 modules in series per row. The wastewater passed through each row of modules, being concentrated in each as it flowed back to the RO feed tank for recycle until the batch was complete. The permeate was collected in the shrouds and flowed into the RO unit product tank.

Spiral-wound membrane configuration--Membranes of cellulose acetate or poly(ether)amide, cast directly on a support sheet, enclosed a product water channel material which was attached to a perforated PVC permeate tube. The other three edges of this laminate were sealed with a waterproof cement. A mesh spacer which provided a uniform flow channel across the membrane was placed on this laminate, and the assembly was wound in a spiral around the perforated rod. Each module contained approximately 80 ft^2 of membrane surface. Three such modules, equipped with peripheral brine seals, were connected in series and slipped into a 10.2-cm (4-in) phenolic-lined steel pipe, which acted as a pressure vessel. The unit consisted of two of these assemblies connected in series.

During operation, feedwater entered the upstream end of the first vessel and flowed axially through the first module. Some purified water flowed through the membrane, down the porous

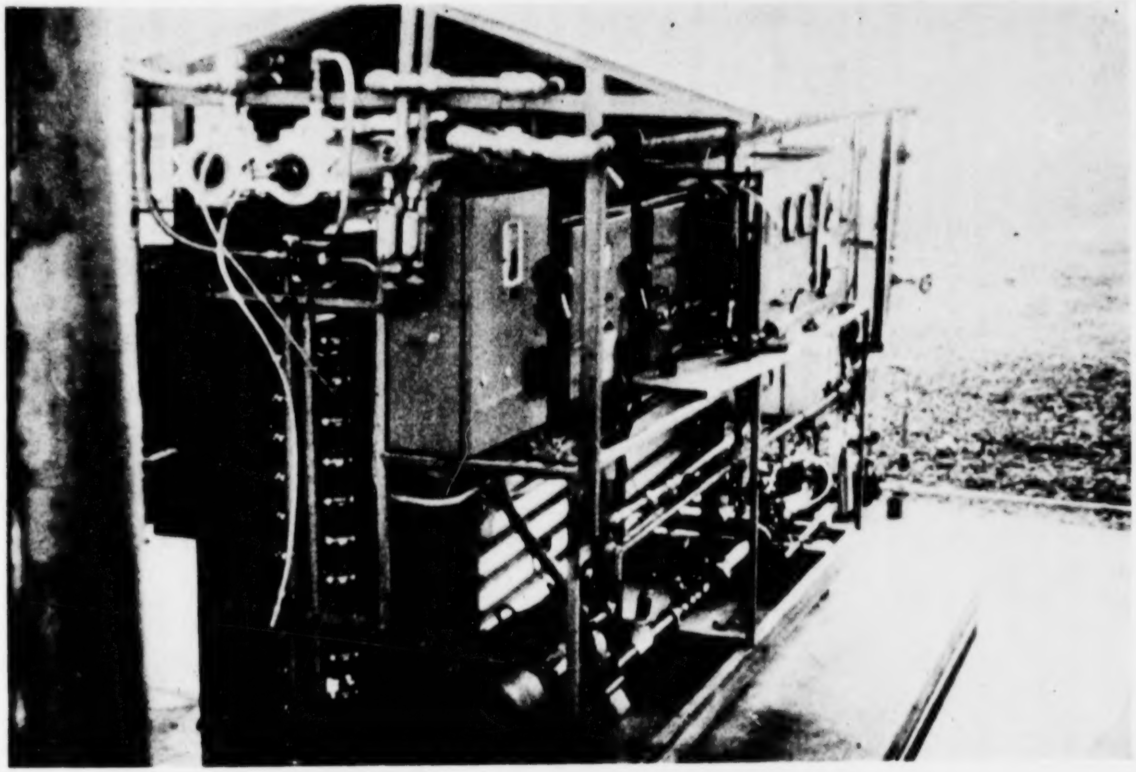

Figure 6. Reverse osmosis unit.

backing and into the central permeate tube. Brine passed through each module, in series, becoming more concentrated as permeate was removed. The brine flowed back to the RO feed and recycled until the batch was completed. The permeate from each module flowed through the central tube and out of the pressure vessel. Permeate from both pressure vessels combined to form the RO product water.

Primary Deionizer--

The primary deionizer was a pre-assembled unit purchased from Illinois Water Treatment Co. (Figure 7). The unit consisted of a 41-cm (16-in) by 183-cm (72-in) resin container, complete with all valves, piping, and controls for completely automatic operation and regeneration. The resin bed contained 0.20 m^3 (7.0 ft^3) of weak-base anion resin intended to remove the residual organics which might foul the resins in the following secondary deionizer unit. The weak-base resin also removed the strong anions. Effluent from the primary deionizer was accumulated in an intermediate (fiberglass) storage tank which supplied feed for the secondary deionizer as well as regeneration cycle rinse water for the primary deionizer.

The resin bed was regenerated with a weak caustic solution which was discharged to the sewer.

Secondary Deionizer--

The secondary deionizer was also a pre-assembled package unit purchased from IWT and similarly equipped for automatic operation and regeneration (Figure 8). The exchanger was a 20-in by 72-in vessel containing 0.07 m^3 (2.4 ft^3) of strong-acid cation resin and 0.14 m^3 (4.8 ft^3) of strong-base anion resin. This mixed-bed treated 5.7 lpm (1.5 gpm) of water from the intermediate storage tank for removal of the remaining total dissolved salts. The demineralized water then flowed to a 7,570 l (2,000 gal) fiberglass storage tank for use as boiler feedwater, dilution water, and deionizer regeneration cycle rinse water.

When the dissolved-salt concentration in the effluent from this mixed-bed unit reached the maximum permissible conductivity, the ion exchanger units were regenerated by an automated backwash, regenerant, and rinse cycle, and then were air mixed prior to returning the unit to service. The cation resin was regenerated with sulfuric acid, and the anion resin was regenerated with caustic simultaneously. The water from the backwash and rinse cycles was also sewered.

Waste Sludge and Backwash Handling

This system consisted of a series of collection tanks and a clarifier for handling the waste sludge and backwash streams from the biological and physical-chemical treatment systems. Waste

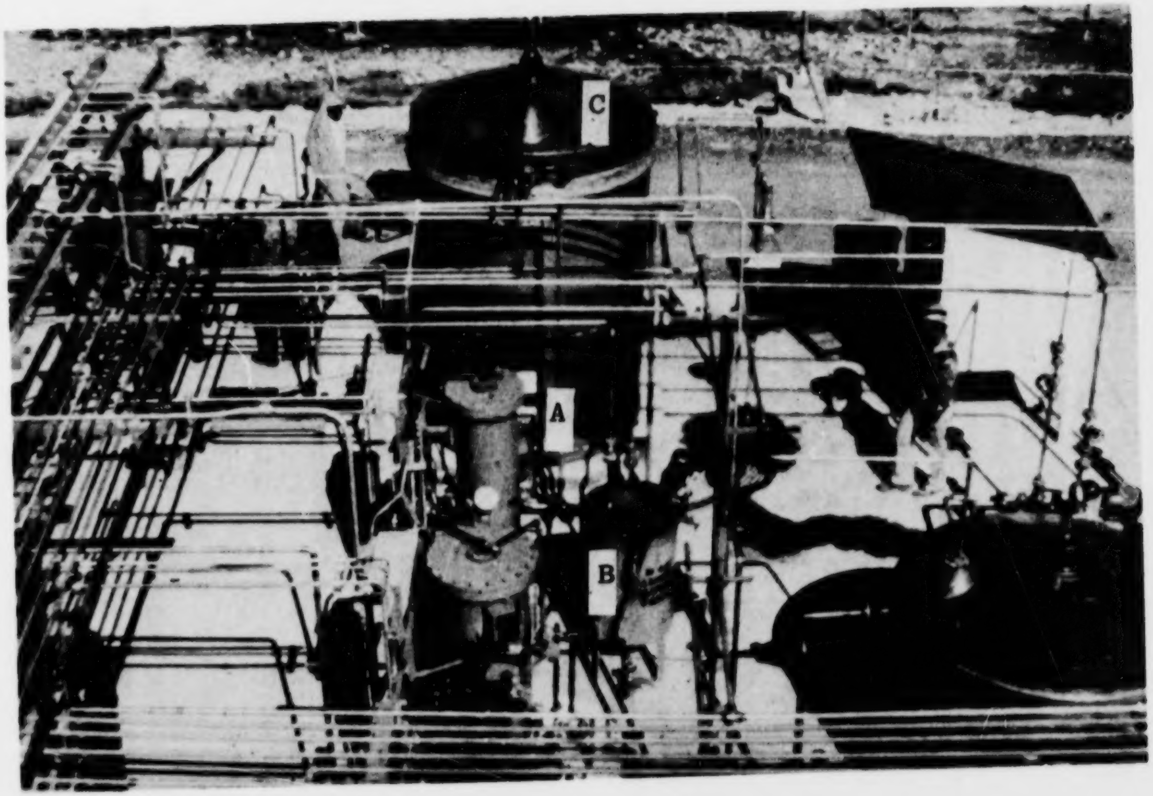

Figure 7. Ion-exchange columns showing weak-base anion column (A) and mixed bed column (B). Fiberglass tank in background (C) stored the renovated water to be fed to the boiler.

sludge from the biosystem clarifier and the sedimentation/filtration unit, plus spent backwash water from the sedimentation/filtration unit, carbon columns and the multi-media filter were piped to a 9,463-l (2,500-gal) tank where coagulants could be added and blended. The wastewater then flowed by gravity to the center well of a 3.7-m (12-ft) diameter clarifier (Figure 8). Clarified effluent flowed by gravity from the clarifier to a 2,271-l (600-gal) tank, from which, depending upon the quality, the clarified water was recycled to the bioreactor, the micro-solids removal unit or discharged to the sewer for ultimate disposal. Sludge from the clarifier was transferred to a 379-l (100-gal) tank for measurement before disposal.

OPERATION OF EXPERIMENTAL FACILITIES

The wastewater renovation pilot facilities were operated on a continuous flow basis receiving pH adjusted, clarified, and equalized wastewater from existing primary treatment facilities. Primary treatment consisted of neutralization, clarification, and 24-hr equalization. Wastewater was pumped continuously from the equalization basin discharge pump to the pilot plant at the rate of 7.5 gpm.

The pilot activated sludge facility was constructed based on a very conservative design to produce the best possible secondary effluent available from a biological facility. Since the pilot activated sludge facility was already considered best available technology for BOD removal, it was not a part of the studies covered under the grant. Its operation and performance are, therefore, discussed only briefly. Primary emphasis of these studies was on tertiary treatment technology.

The pilot facilities were operated, maintained, and supervised by UCCI plant personnel with technical assistance from a research and development technician on site. Routine wastewater analyses required for daily operational changes were performed by the shift operators. All analytical analyses on routine samples were conducted by plant laboratory personnel.

Activated Sludge

Average operating conditions over the entire study for the activated sludge system are summarized in Table 1.

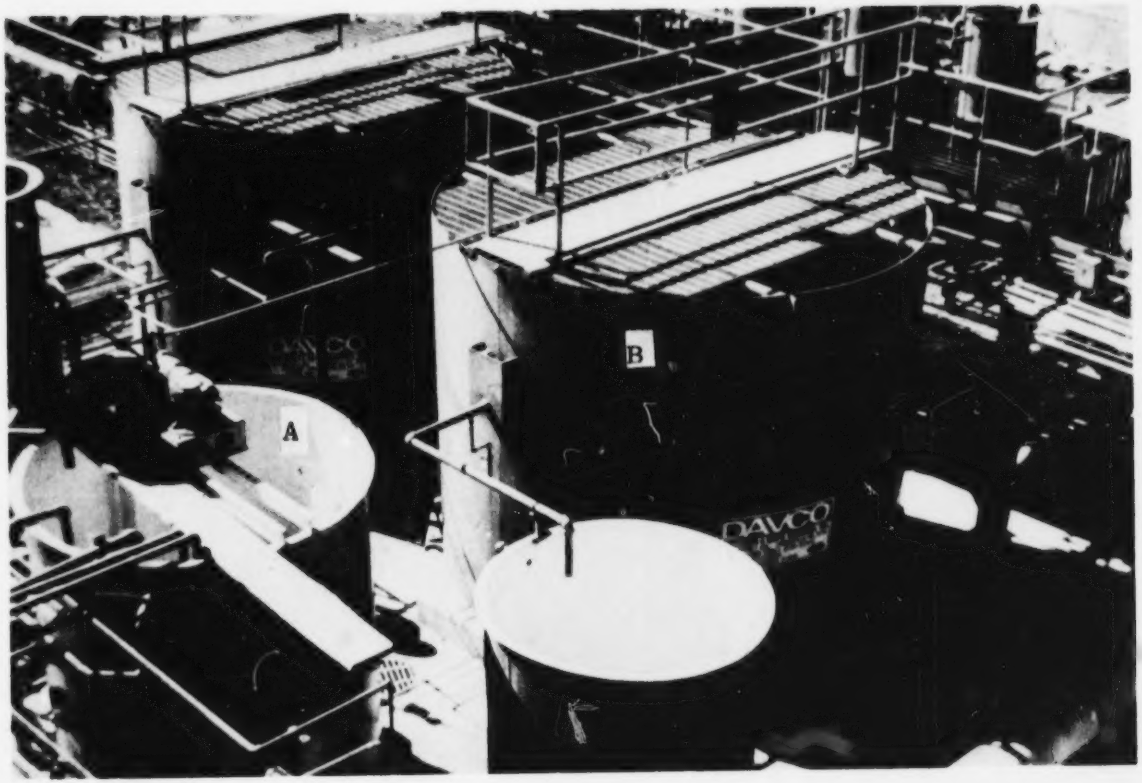

Figure 8. Waste sludge and backwash handling system showing waste collection tank with mixer (A) and 12-ft-diameter clarifier (B).

TABLE 1. AVERAGE OPERATING CONDITIONS FOR ACTIVATED SLUDGE PILOT FACILITY

Reactor pH	8.15
Reactor temperature	31-34°C (88-93°F)
Retention time	7.58 days
Mixed liquor suspended solids (MLVSS)	2,140 mg/l
Mixed liquor volatile suspended solids (MLVSS)	1,883 mg/l
Recycle suspended solids (RSS)	16,000 mg/l
Clarifier overflow rate	100 gpd/ft^2
Sludge age	55 days
F/M applied	0.18 lb BOD/day/lb MLVSS
Basin dissolved oxygen	2.0 to 4.0 mg/l

As a routine procedure whenever an inlet total organic carbon (TOC) greater than 5,000 mg/l, or phenol greater than 200 mg/l was indicated, flow was diverted to the panic pond. Normally, these high peaks lasted only a short time and as the concentration dropped below these levels, normal flow through equalization was resumed. Wastewater collected in the panic pond was then slowly bled back into the equalization basin.

Polyelectrolytes or coagulants were not added to the secondary clarifier, though facilities to do so were available. The very conservative size of the clarifier and already good settling characteristics of the mixed liquor did not warrant the addition of these flocculant aids. Sludge was recycled and wasted continuously from the clarifier underflow to maintain a sludge age of 50 days.

Bio-treated and clarified wastewater was then used as feed to the subsequent tertiary treatment facilities.

Sedimentation/Filtration Unit

This unit processed 22.7 to 26.5 lpm (6.0 to 7.0 gpm) of clarified bio-effluent for the removal of suspended solids. Polyelectrolytes and coagulants were not used throughout the study as a result of lower solids loading than expected and satisfactory clarification and filtration without the use of these chemicals.

The unit received flow continuously. Solids were removed intermittently from the bottom of the primary and secondary settling tubes during filter backwash. The multi-media filter. operating at a hydraulic loading of 142.5 lpm/m^2 (3.5 gpm/ft^2) was backwashed, automatically or manually, when the filter effluent pump suction exceeded 10 inches mercury vacuum. Backwash frequency was approximately once per shift at 45.4 lpm (12 gpm) for 8 minutes.

Effluent from the sedimentation/filtration unit was collected in the carbon adsorption feed tank. This tank had a continuous overflow to insure variable feed to the carbon columns.

Activated Carbon Adsorbers

Three beds in series were operated in an expanded upflow mode. The adsorbers received flow continuously at 18.9 lpm/m^2 (5 gpm/ft^2). Carbon contact time through the three-bed sequence was 100 minutes (0.59 BV/hr overall).

The operating sequence for this three-bed series adsorption system was as follows: Three beds were placed on-line in series operation after being charged with virgin carbon. Feed and effluent COD for each column were monitored closely on 24-hour composite samples. At the point when the effluent from the last column in series exceeded some maximum acceptable level (arbitrarily chosen in this case to be the 60 percent COD rejection level), the lead column was taken off line for regeneration--the second and third columns were advanced to the lead and second position, and a fresh column, charged with virgin carbon,was placed in the terminal position. These columns were kept on-line until the minimum acceptable COD removal (60 percent) was again reached. At this time the lead column was removed, and the process was repeated. A total of 6 carbon beds were exhausted in these studies.

Throughout these studies virgin carbon was used for all column charges. Exhausted carbon was regenerated in vendor's laboratories and analyzed for comparison to virgin carbon.

When the pressure drop across any column exceeded 20 psig, the column was backwashed for about 15 minutes at 45.4 lpm (12 gpm) to remove the accumulated solids. Backwash water was supplied from the adsorber effluent tank that stored effluent from the multi-media pressure filter following the carbon adsorption unit. Spent backwash water was piped to the waste sludge and backwash collection tank.

Multi-Media Filter

The multi-media filter bed received 18.9 lpm (5 gpm) flow directly from the last carbon adsorber in series, entering the top of the bed at 10 to 15 psig. When the pressure drop across the bed exceeded 8 psig, the operator placed the filter in backwash for 10 to 15 min at 34.1 lpm (9 gpm) to expand the bed and remove the accumulated solids. Spent backwash was piped to the waste sludge and backwash collection tank. Backwash was done manually, approximately once per shift, and the unit was placed immediately back in service.

Reverse Osmosis Unit

Cellulose acetate (CA) membranes in the tubular configuration, CA and polyamide (PA) membranes in spiral-wound configuration were each operated at one point in these studies. Operating conditions varied somewhat with each membrane used.

Tubular Cellulose Acetate Membrane--

Initial operation of the RO system utilized the tubular configuration with cellulose acetate membranes. These modules operated up to 600 psig inlet pressure with a pressure drop of 200 to 250 psig across the membrane surface. An 87.1 lpm (23 gpm) feed rate resulted in 30.1 lpm (8 gpm) of permeate flow; the remaining 56.8 lpm (15 gpm) concentrate flow was recycled back to the feed tank. Maximum allowable feed temperature set by the manufacturer was 43.3°C (110°F). Feed pH was maintained between 4.0 and 5.0 by adjustment of acid feed pumping rate.

When permeate flow began to drop at 600 psig inlet pressure, the membranes were flushed with demineralized water. When this failed to restore permeate flow, the system was flushed with one of two recommended cleaning solutions (Table 2) and rinsed with demineralized water prior to being placed back in service. When the unit was inoperative for short periods of time the modules were flushed with demineralized water adjusted to a pH of 4.0 to 6.0. When inoperative for more than 100 hours, a solution containing 0.5 percent formaldehyde was maintained in the modules.

RO permeate was collected in a covered tank which had a continuous overflow.

Spiral-wound Cellulose Acetate Membranes--

These modules were operated under conditions similar to the tubular membrane configuration, except maximum inlet pressure was reduced to 500 psig with an 80-psig pressure drop across the membrane. Total flow through the unit was reduced to 22.7 lpm (6 gpm) permeate and 22.7 lpm (6 gpm) concentrate return. The same pH adjustment and membrane cleaning procedures were followed as with the tubular configuration. Shell-in-tube heat exchangers were added to the concentrate return in an attempt to keep the temperature below 43.3°C (110°F).

TABLE 2. CLEANING SOLUTIONS FOR RO MEMBRANES

Solution A - Iron or Heavy Metal Fouling	
Deionized Water	45 gal
Citric Acid	7.5 lb
Triton X-100 (Rohm and Haas)	175 ml
Carboxy Methyl Cellulose	2.5 gm
NH_4OH to Adjust to pH	3.0
Formaldehyde (37% formalin)	2,365 ml (Optional)
Solution B - Organic Fouling	
Deionized Water	45 gal
Sodium Tripolyphosphate	7.5 lb
Sodium EDTA (powder)	3 lb
Carboxy Methyl Cellulose	2.5 gm
Triton X-100 (Rohm and Haas)	175 ml
H_2SO_4 to adjust pH to	6.0 (4160 HR elements) 10.0 (polyamide elements)
Formaldehyde (37% formalin)	2,365 ml (Optional)

Spiral-wound Polyamide Membranes--

The module configuration was the same as the CA spiral-wound modules with the same operating flows and pressures. Polyamide membranes, with a maximum allowable temperature of 57.2°C (135°F), operated safely at 48.9°C (120°F). The pH tolerance of this membrane (pH of 3.0 to 9.0) enabled operation with or without pH adjustment.

Primary Deionizer

The primary deionizer was operated intermittently to produce water free of any residual organics for the secondary deionizer. Water from the RO product tank was pumped through the bed at 18.9 lpm (5 gpm) and into the fiberglass intermediate tank. The resin bed was regenerated at the same time as the secondary deionizer. Regeneration involved: 15-min backwash at 26.5 lpm (7 gpm), addition of 4 percent caustic solution, slow rinse at 11.4 lpm (3 gpm) and fast rinse at 22.8 lpm (6 gpm). Final rinse was complete when the rinse water effluent reached a pH of 9.5 or less. The resin bed was then ready for service. All flows during regeneration were sewered.

Secondary Deionizer

The secondary deionizer was operated intermittently to produce deionized hardness-free boiler feedwater. When in service, a 56.8 lpm (15 gpm) flow was passed through the mixed bed with 51.1 lpm (13.5 gpm) recycled back to the intermediate tank, and 5.7 lpm (1.5 gpm) of effluent was passed to the boiler feedwater storage tank. The resin bed was considered exhausted when the effluent exceeded 1.0 µmho conductivity. At this level, an alarm sounded, and all effluent automatically diverted to the sewer.

Regeneration of the mixed bed was done manually and involved several steps:

1. Blowdown to lower water level for backwash.
2. 15-min backwash to separate anion and cation resins.
3. 2 percent H_2SO_4 fed for 15 min, followed by H_2SO_4 for 15 min to convert cation resin to hydrogen cycle.
4. 4 percent caustic solution fed to convert anion resin.
5. 18.9 lpm (5 gpm) slow rinse for 15 min.
6. 47.3 lpm (12.5 gpm) fast rinse for 20 min.
7. Air-water mix to blend the resins.
8. Air drain to settle the mixed resins.
9. Final rinse until resin bed is the desired purity.

All caustic, acid and water utilized in regeneration were discharged to the sewer.

SAMPLING AND ANALYSIS

Routine Samples

Grab samples of feed and effluent from each of the wastewater renovation unit operations were taken every 4 hours and combined to form a 24-hr composite. Samples were kept refrigerated and sent to the plant laboratory each morning for analysis. The wastewater analyses listed in Table 3 were conducted according to Methods for Chemical Analysis of Water and Wastes (1) and Standard Methods for the Examination of Water and Wastewater (2).

TABLE 3. ROUTINE WASTEWATER ANALYSES CONDUCTED ON 24-HOUR COMPOSITE SAMPLES

Biochemical Oxygen Demand (BOD_5)	pH
Chemical Oxygen Demand (COD)	Specific Conductance
Total Organic Carbon (TOC)	Total Dissolved Solids (TDS)
Volatile Suspended Solids	Iron
Phenol	Silica
	Chloride

Not all analyses were run on every sample. For example, the emphasis on the filters was suspended solids; on the carbon columns the emphasis was COD; and the emphasis on demineralization units was conductivity. Analyses performed on specific samples are shown in the tables referred to in the section RESULTS AND DISCUSSION.

Special Samples

Waste secondary sludge and backwash waters from the sedimentation/filtration unit, carbon columns and mixed-media filter were sampled periodically and analyzed for solids and heavy metals content. Grab samples were taken when the units were considered in normal operation. Samples for COD and suspended solids were collected in glass bottles; samples for metals analyses were collected in polyethylene bottles and fixed with 5 ml of concentrated nitric acid per liter of sample. Metals analyses were conducted by atomic adsorption and flame UV, after digestion of the samples and after returning the samples to original volumes. Analyses of the original samples are expressed as mg/l.

Demineralization System--

Grab samples of the RO feed and permeate and ion exchange columns feeds and effluents were taken periodically for additional analyses. Samples were collected in polyethylene bottles and analyzed for specific anions and cations. These analyses were not critical to the operation of the demineralization facilities but were needed for characterization of the wastewater.

Waste Brines--

Reverse osmosis brine and the regeneration brines from the ion-exchangers were sampled and analyzed periodically in the same manner as the waste sludges were for solids and heavy metals content. The RO brine was sampled after a batch had finished being concentrated and the brine was dumped to the sewer. The ion-exchange regeneration brines were sampled several times during each cycle in the regeneration sequence and composited according to flow to obtain a sample representative of the total brine to be discharged.

Specific Organics--

A 24-hr composite sample was taken of the effluent from the equalization basin, sedimentation/filtration effluent, carbon adsorption, RO and ion-exchange effluents, for gas chromatographic analysis for specific organics. The samples were shipped to research and development laboratories in South Charleston, West Virginia, for analysis. The analytical procedures employed were among those generally accepted for the analysis of specific compounds in wastewater; and, in the case of the concentrating procedure, it was that procedure recommended by EPA (3,4). These procedures are detailed in Appendix A.

RESULTS AND DISCUSSION

Treatment Performance

As previously stated, the pilot activated sludge basin and clarifier were constructed only to produce high quality secondary effluent. As such, they are not a part of these studies covered by the EPA grant and the operation and performance of these units will not be discussed in detail.

The pilot activated sludge system was a very conservative design--long retention time, low clarifier overflow rate, and ample oxygen supply to meet any conceivable influent demand. The system was carefully operated to exclude spills, upsets in nutrient supply, and surges in hydraulic flow-rate. The constant semitropical ambient temperature and the inherently high amenability of the raw wastewater from this plant to bio-treatment favored a high level of performance in the pilot activated sludge system. The biological effluent average BOD, COD, and suspended solids levels for the study period were 31 mg/l, 184 mg/l, and 44 mg/l, respectively (Table 4). The consistent achievement of a high degree of biological treatment was critical to the successful performance of the downstream tertiary treatment systems in the actual water renovation pilot plant. Excessive variability in the bio-effluent could have led to erratic performance of the suspended solids removal system, rapid breakthrough in the carbon adsorbers, excessive filter backwash requirements, and possible fouling in the reverse osmosis-ion exchange units. In fact, these potential problems were largely absent due to the consistent performance of the pilot activated sludge system.

Sedimentation/Filtration Unit--

The sedimentation/filtration unit averaged approximately 70 percent suspended solids removal decreasing the suspended solids from an average 45 mg/l to 13 mg/l (Figure 9). Some COD reduction 20 to 25 percent, was observed across the unit. COD measurements were made on unfiltered samples and, therefore, the observed reduction is throught to be primarily insoluble COD--mostly in the form of bacterial solids.

Suspended solids levels generally experienced in secondary effluents from organic chemical wastewaters are on the order of 100 to 200 mg/l and often exhibit poor settling and filtering characteristics. The low solids levels and the ease with which these solids were removed make an evaluation of this unit difficult. Effluent from the sedimentation/filtration unit was fed directly to the activated carbon columns.

Activated Carbon Adsorption--

The variability in COD load to the carbon columns was relatively small due to the equalizing effect of primary and secondary treatment steps. Feed to the carbon columns averaged 140 mg/l COD. The final effluent from the three beds in series operation was consistently below 50 mg/l total COD (Figure 10). An average 71 percent COD reduction was achieved with virgin carbon (Figure 11). The lead bed in the series was exposed to the more readily adsorbed organics and, therefore, removed a higher percentage of the organics than the two trailing beds, except when the lead bed approached exhaustion at which point the second bed in series showed a higher percentage COD removal.

TABLE 4. ACTIVATED SLUDGE EFFLUENT SUMMARY
WEEKLY AVERAGES
PILOT PLANT BIOLOGICAL EFFLUENT

Date	BOD mg/l	COD mg/l	TOC mg/l	SS mg/l	Phenol(1) mg/l
4/3-9	22	-	134	61	-
10-16	18	-	78	50	-
17-23	18	-	50	29	-
24-30	21	-	86	29	-
5/1-7	16	80	90	46	0
8-14	54	90	127	47	2.4
15-21	16	121	64	43	0
22-28	12	127	78	30	0.9
29-6/4	19	100	65	21	2.3
5-11	32	100	39	23	0
12-18	76	249	105	60	0
19-25	18	119	99	48	0
26-7/2	62	128	-	35	0
3-9	48	170	-	47	0
10-16	15	101	-	23	0.7
17-23	6	104	-	30	1.2
24-30	-	149	-	28	0
7/31-8/4	17	243	-	72	0
5-11	65	134	-	62	0
12-18	25	147	-	66	0.25
19-25	34	149	-	68	0.26
26-9/1	50	158	-	63	0
2-8	34	147	-	43	0.75
9-15	16	151	-	43	0
16-22	23	143	-	46	0
23-29	-	139	-	43	0
30-10/6	19	147	-	40	0.3
7-13	24	109	-	24	0
14-20	12	124	-	29	0
21-27	82	140	-	25	0
27-11/3	78	149	-	27	
4-10	10	145	-	36	0
11-17	36	228	-	72	0
18-24	23	228	-	73	0
25-12/1	24	246	-	81	0
2-8	75	340	-	91	0
9-15	10	205	-	64	0
16-18	-	196	-	58	0
AVG.	31	184	-	44	0.27

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(1) Less than detectable limit of test (0.1 mg/l) is recorded as 0.

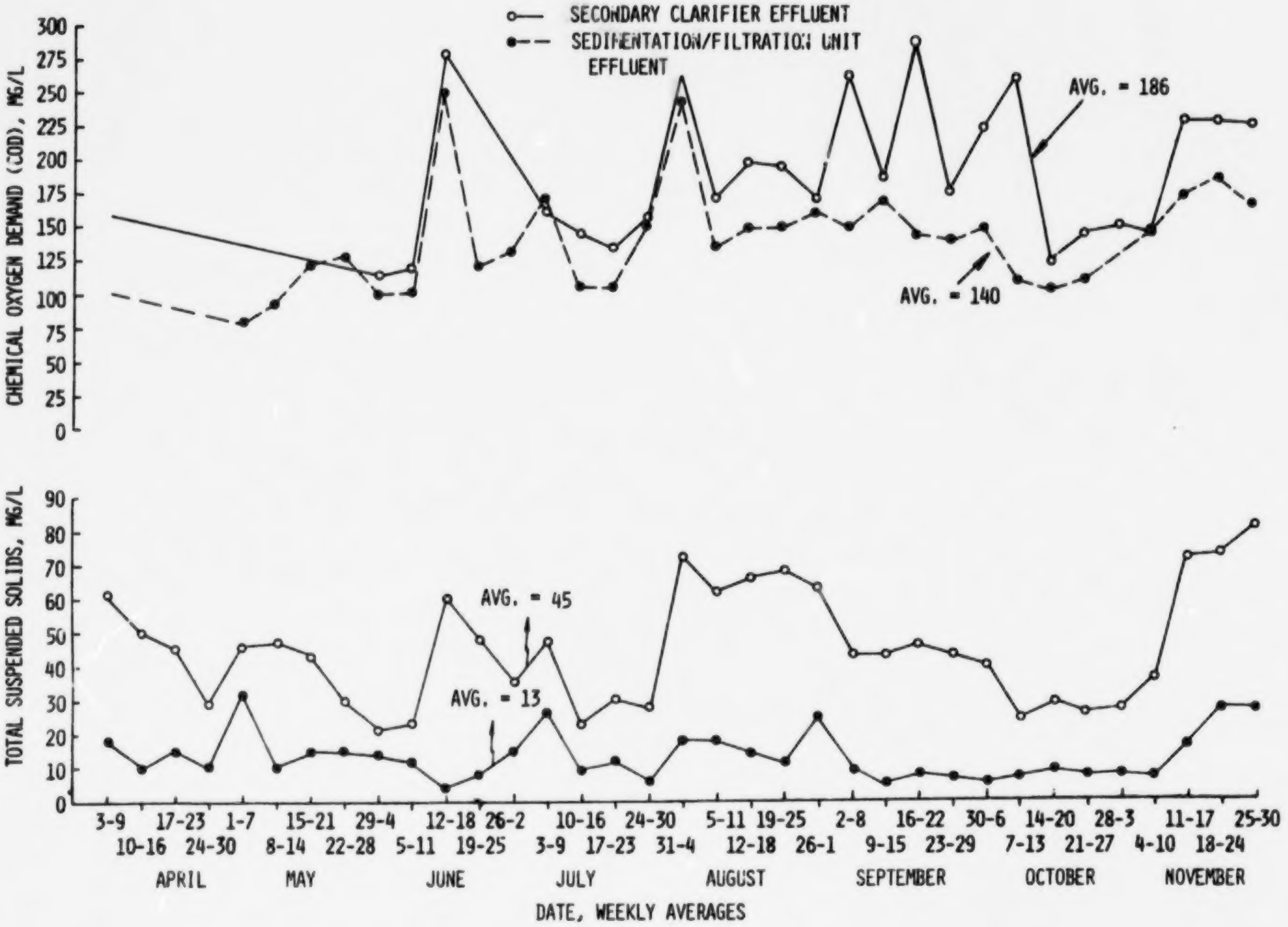

Figure 9. Sedimentation/Filtration unit performance data.

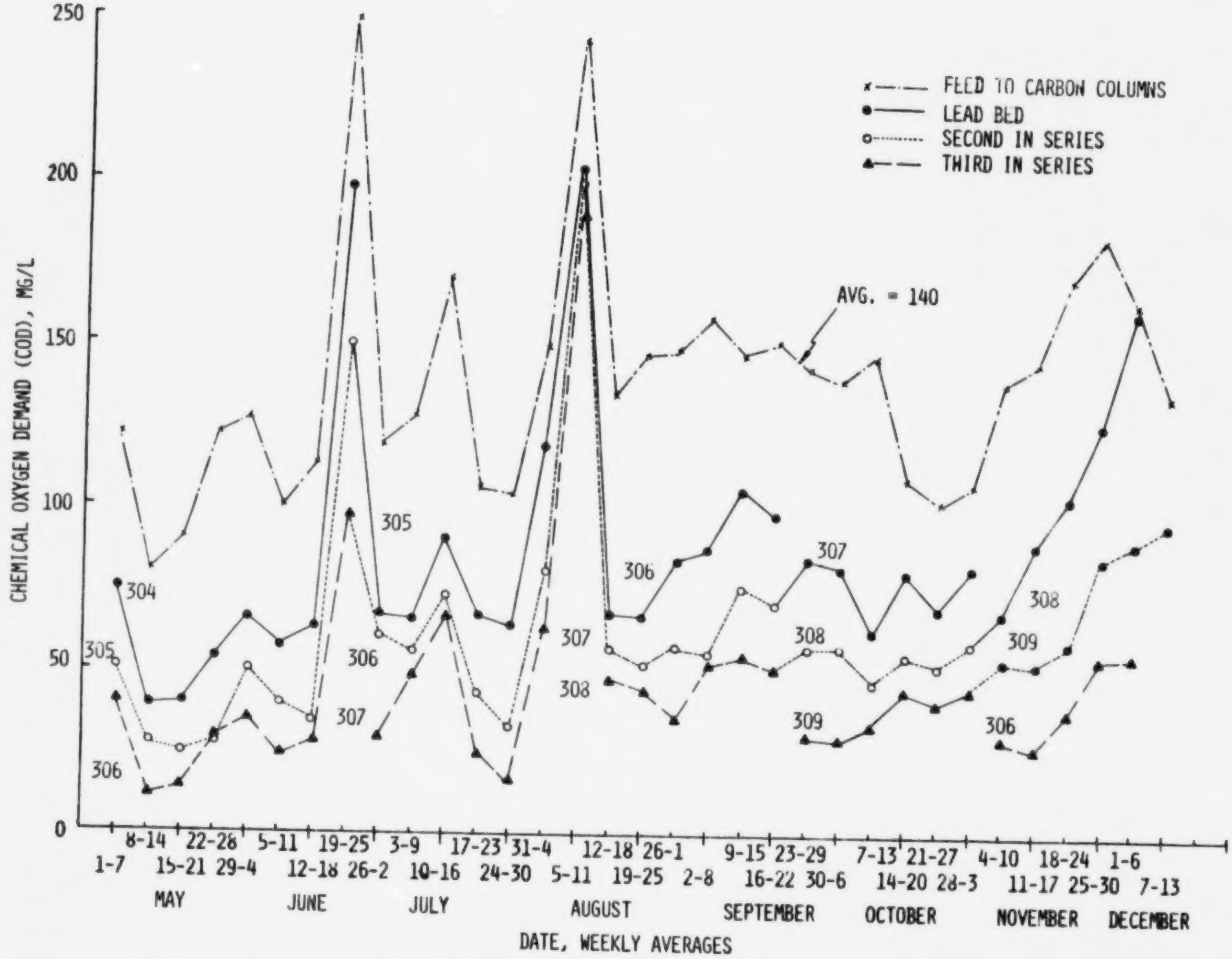

Figure 10. Activated carbon column COD data.

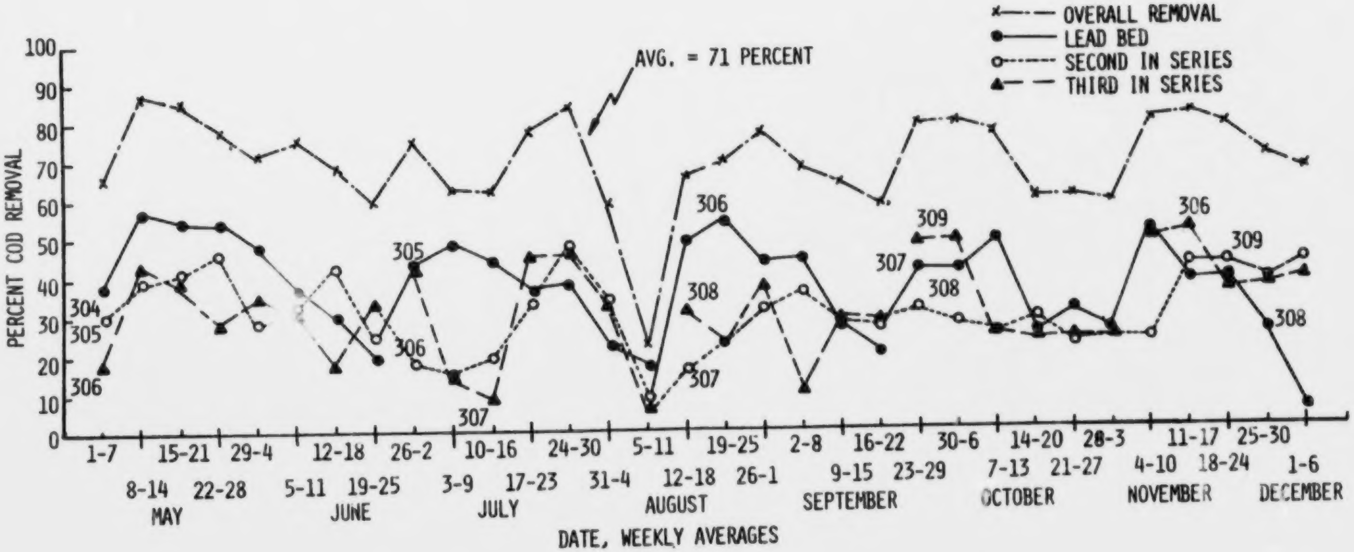

Figure 11. Activated carbon columns percent COD removal based upon feed to and effluent from each column.

A total of five carbon beds containing virgin granular carbon were exhausted at an average loading of 0.352 gram (gm) (pound (lb)) of COD per gm (lb) of carbon. A sixth bed, taken off line at the end of the studies, approximately one week before exhaustion, was loaded to 0.275 gm (lb) of COD per gm (lb) of carbon. Breakthrough curves plotted as the fraction of feed COD remaining in the effluent from each column, along with the final carbon loadings are shown in Figure 12. Cumulative carbon loadings (Figure 13) as well as the breakthrough curves (Figure 12) indicate that the carbon adsorption unit operated classically with smooth breakthroughs, regular time periods between column exhaustions, and consistent carbon loadings.

Activated Carbon Regeneration--

Carbon column #304 was operated continuously as the lead bed in the series adsorption system from April 14 to June 25 (COD data were not taken in April). During this period of operation, the COD removal efficiency of the carbon decreased from 57 percent to 19 percent, and the carbon adsorbed 0.311 gm (lb) COD/gm (lb) carbon. A sample of the exhausted carbon was removed from column #304, air-dried, and approximately 11.3 kilograms (kg) (25 lb) were submitted to the Calgon Corporation Laboratory in Pittsburgh for reactivation tests.

After reactivating a small aliquot in a laboratory furnace, the bulk of the sample was reactivated in a pilot-scale rotary kiln. The reactivation restored 98 percent of the carbon's iodine number, 92 percent of the molasses number, and increased the ash content by 62.6 percent (from ~8 percent to 13 percent), compared to minimum specifications for virgin Calgon carbon (Table 5). While the carbon losses on reactivation in the rotary kiln were quite attractive, 4 percent vs. 5 to 15 percent losses reported in the literature, this parameter cannot be extrapolated from one furnace to another.

As an additional check on the behavior of the carbon during reactivation, the returned reactivated carbon was analyzed for pore size distribution using the Digisorb 2500 analyzer. Results shown in Table 6, compare to a similar analysis for virgin Filtrasorb 400 (similar to, but not necessarily identical to Filtrasorb 300). Thermal regeneration reduced the carbon B.E.T. surface area by ~25 percent, decreasing the surface area in pores $\leq$50 angstroms in diameter and increasing the surface area in larger pores. Loss of surface area resulted from burnout of interstitial carbon and from accumulation of ash that choked off smaller pores.

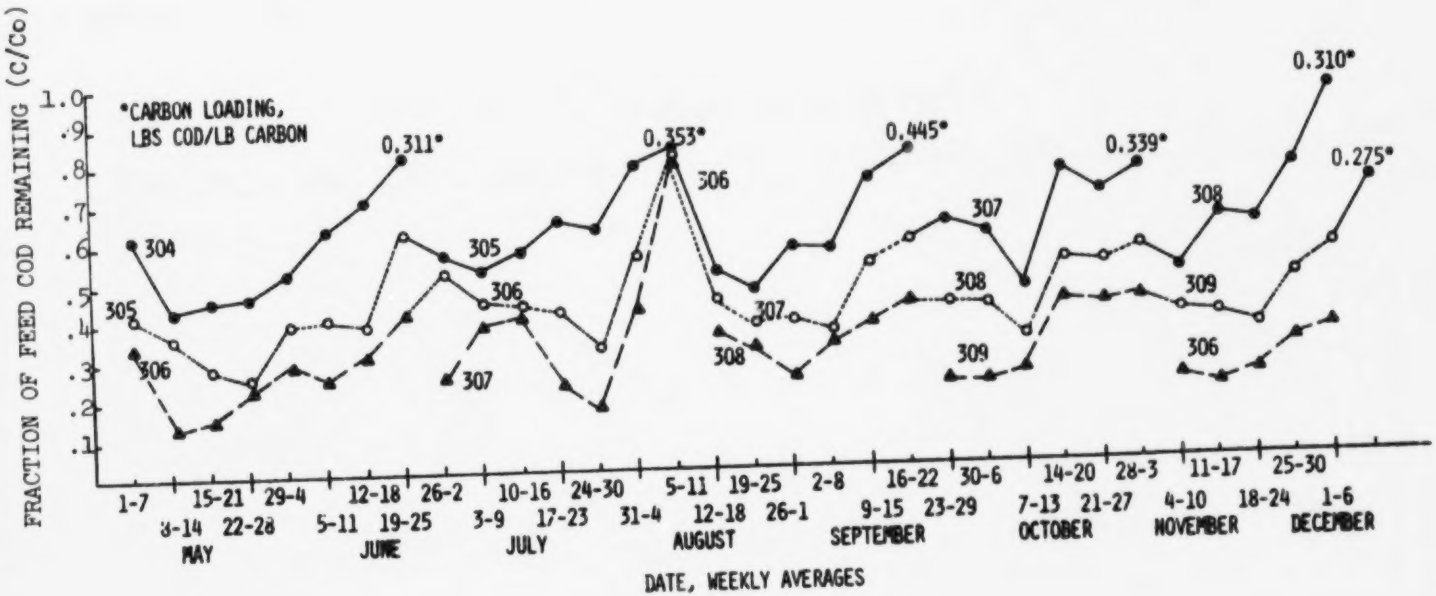

Figure 12. COD breakthrough curves - fraction of feed COD remaining (C/Co).

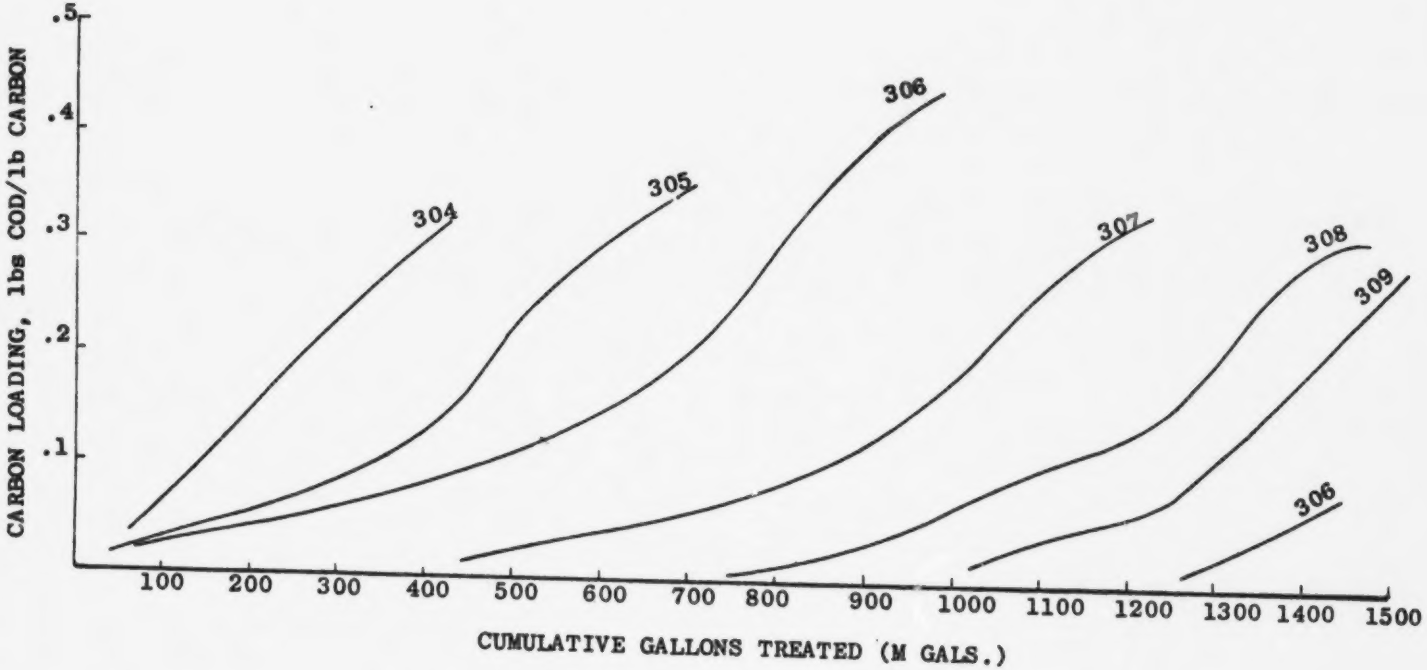

Figure 13. Activated carbon column cumulative carbon loadings based upon COD.

TABLE 5. SPENT CARBON REACTIVATION TESTS

	SPENT	LABORATORY REACTIVATED	PILOT-SCALE ROTARY KILN REACTIVATED	TYPICAL VIRGIN CARBON(1)
Apparent Density, Air Dried	0.670	-	-	-
Apparent Density, Dried 150°C	0.608	-	-	-
Apparent Density, Reactivated	-	0.478	0.456	0.48
Iodine Number	581	845	886	900-975
CCl_4 Number	23.8	47.9	51.3	-
Molasses Number	231	324	367	~400
Ash (%)	8.90	11.50	13.01	5-8.0
Time (Minutes)	-	.1	35	-
Temperature			1700° - 1800°F	

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(1) Based on telephone conversation with Mr. Talli at Calgon.

TABLE 6. PORE SIZE DISTRIBUTION FOR REACTIVATED AND VIRGIN CARBON
(Digisorb 2500 Analyzer)

Pore Diameter Angstroms	Surface Area, m^2/gm, in Pores of Given Size	
	Reactivated	Virgin
< 20 Å	533.508	758.803
20-30	133.226	198.992
30-40	39.426	44.703
40-50	19.344	19.417
50-60	11.746	9.941
60-80	14.193	10.144
80-100	8.454	4.900
100-150	12.650	5.707
150-200	6.194	2.644
200-300	5.754	2.682
300-400	2.785	1.359
400-500	1.282	0.593
500-600	0.718	0.436
Total B.E.T. Surface Area	789.278	1060.390

The Freundlich isotherm technique was used to compare the performance of reactivated carbon to virgin carbon in batch adsorption tests using pilot-plant bio-effluent after the sedimentation/filtration step. Both carbons were pulverized prior to the test. Carbon dosages from 0 to 20 gm/l were contacted with wastewater aliquots for two hours, filtered, and the filtrates analyzed for TOC and COD. Percentage removals vs. carbon dose are shown in Figure 14. Both carbons performed about equally well. The decrease in percentage COD removal at the higher carbon dosages probably resulted from the indicated pH increase induced by the carbon.

Figures 15 and 16 show Freundlich isotherm plots for the batch adsorption tests. Again, essentially equivalent performance is indicated for both virgin and reactivated carbon. The slope changes in the graphs probably reflect the aforementioned effect of increasing wastewater pH with increasing carbon dose. No loss of adsorptive capacity occurred in the carbon during the exhaustion/reactivation cycle, as indicated by the isotherm values of $(X/M)c_o$:

	mg/gm Carbon	
	Reactivated	Virgin
TOC	185	210
COD	1090	795

The apparent differences result from fitting a line to the data points by eye.

It was concluded that the sample of "exhausted" carbon from the pilot-plant adsorber was restored to near-virgin condition by thermal oxidative regeneration in a rotary kiln at Calgon's Pittsburgh Laboratory. Iodine number, molasses number, and the carbon's performance in batch isotherm tests all indicated this high degree of reactivation.

The furnace operating conditions and observed carbon losses (4% by volume) cannot be directly extrapolated to larger-scale furnace systems. However, this study does indicate that spent carbon from the pilot-plant can be reactivated to near-original adsorptive properties.

Multi-media Filtration--

Effluent from the last carbon column in series flowed directly into the multi-media filter bed. Feed suspended solids numbers are based upon samples taken of the sedimentation/filtration unit effluent and, therefore, do not include any biological solids or carbon fines from the carbon adsorber beds. Feed suspended solids numbers ranged from 5 to 35 mg/l and averaged 13 mg/l. Effluent from the filter ranged from NIL to 20 mg/l and averaged 7 mg/l, approximately 50 percent solids removal (Figure 17). Actual removals were probably considerably

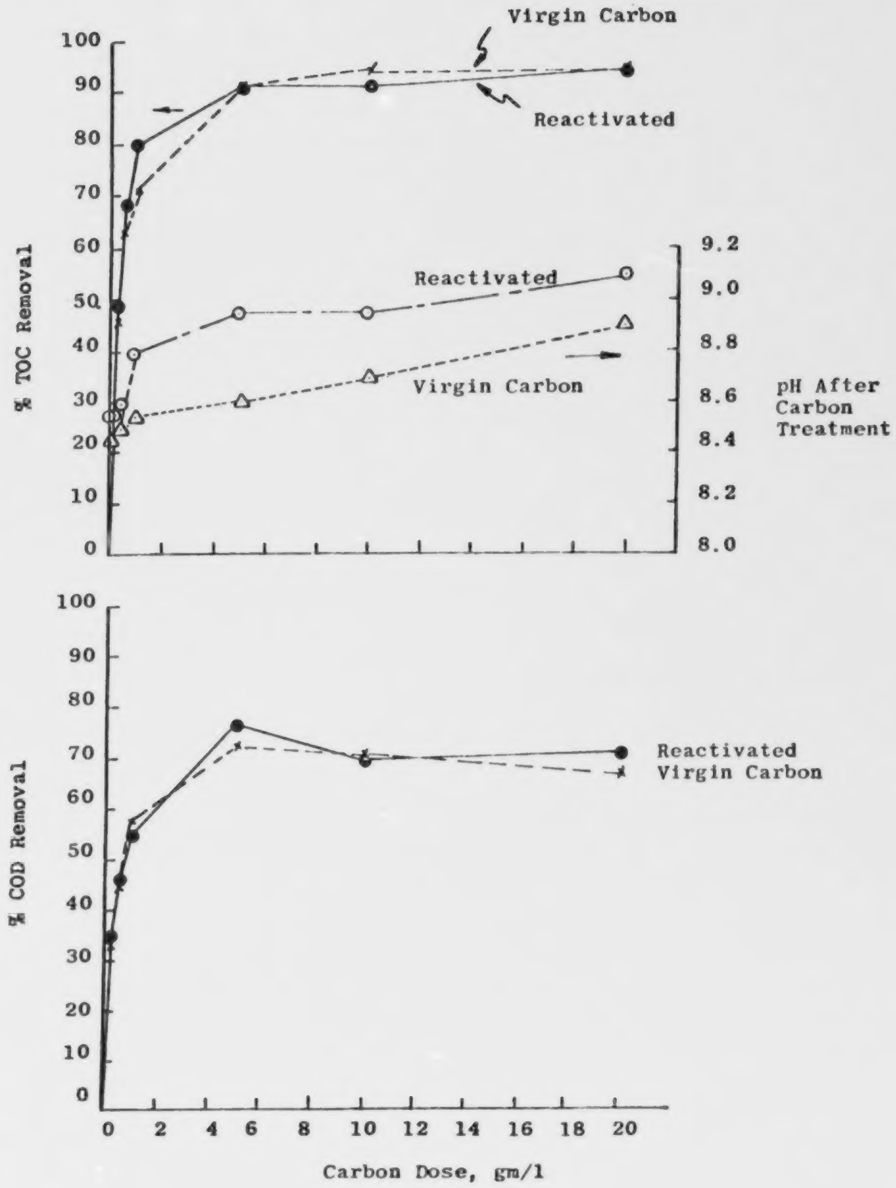


Figure 14. Percent organic removal vs. dosage. Reactivated vs. virgin calgon filtrasorb carbon sedimentation/filtration effluent: TOC = 35 mg/l
COD = 190 mg/l

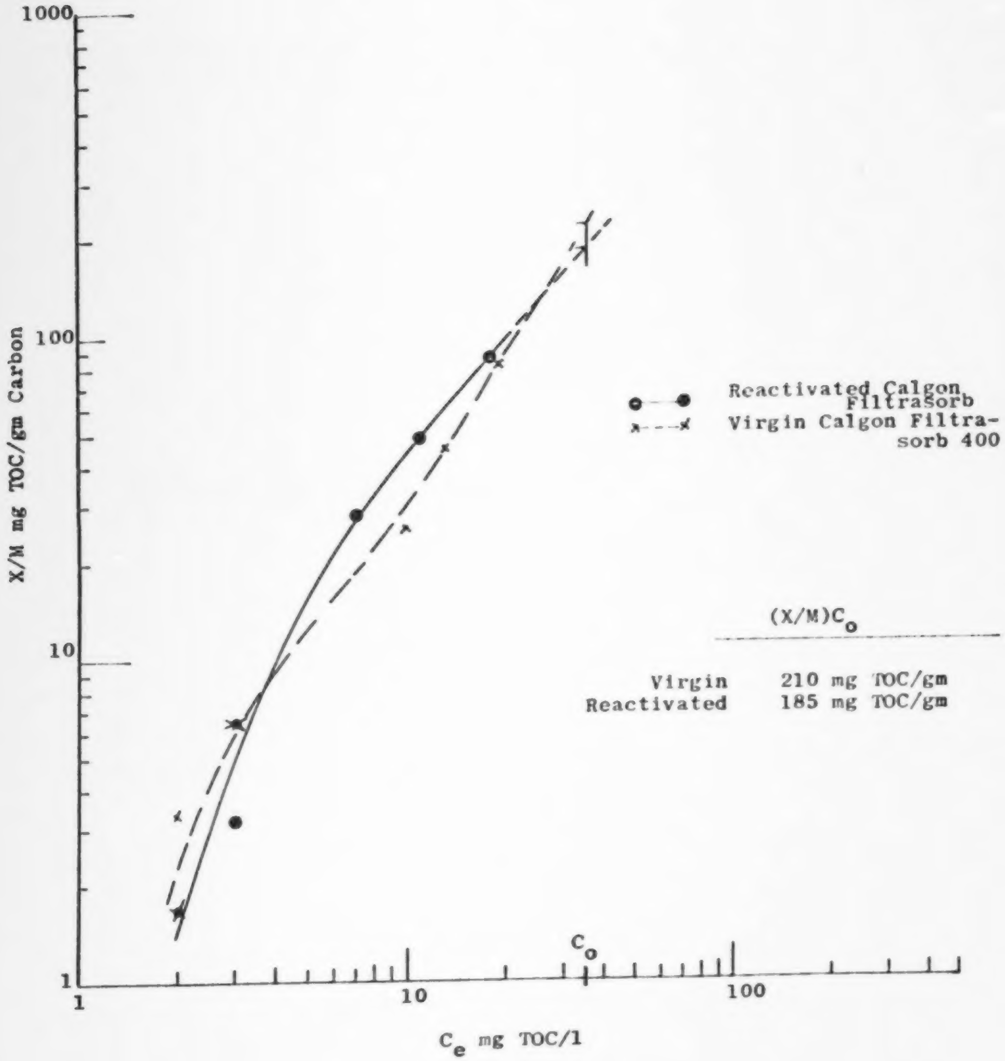


Figure 15. Freundlich isotherm - evaluation of reactivated carbon from pilot col. #304 treating sedimentation/filtration unit effluent.

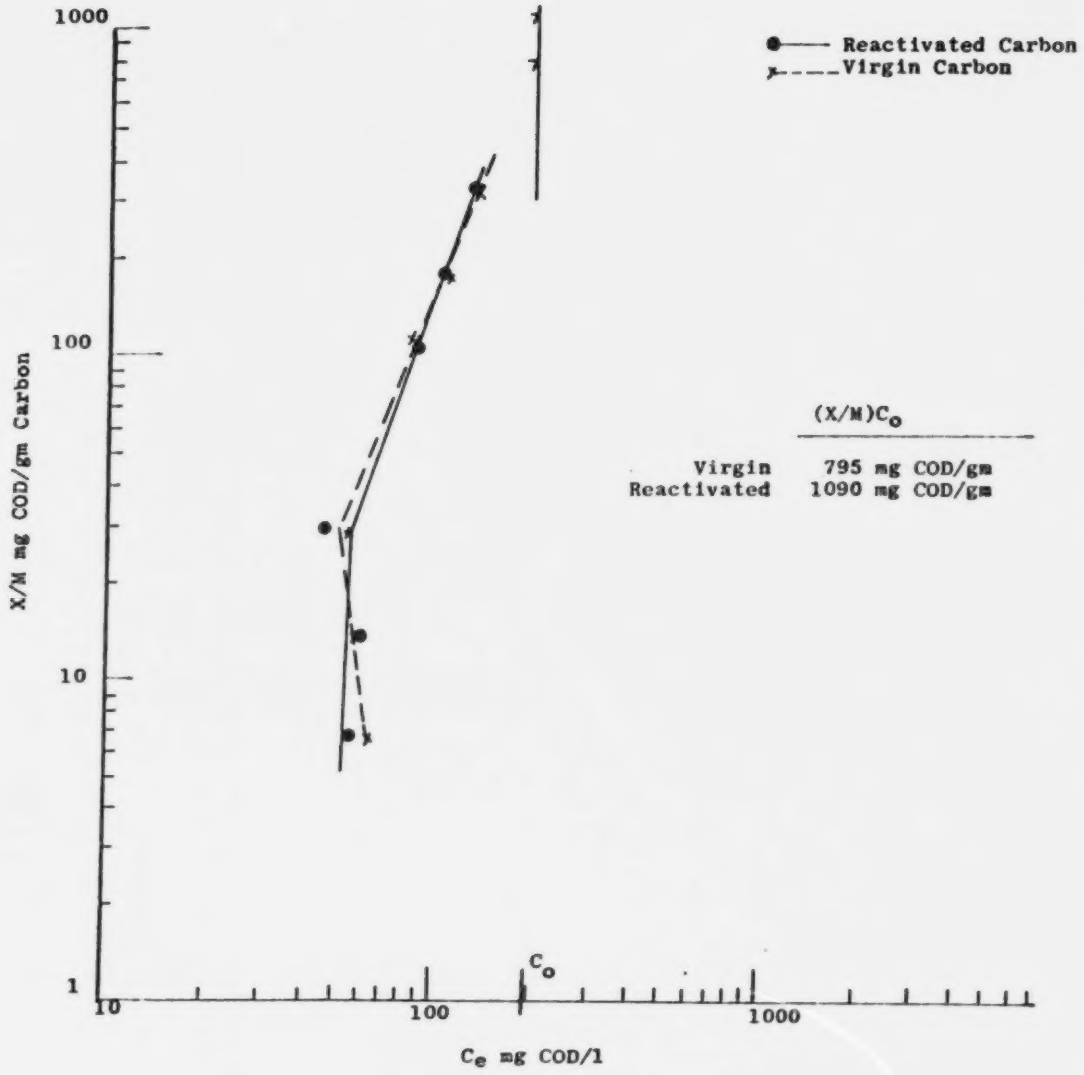


Figure 16. Freundlich isotherm - evaluation of reactivated carbon from pilot col. #304 treating sedimentation/filtration unit effluent.

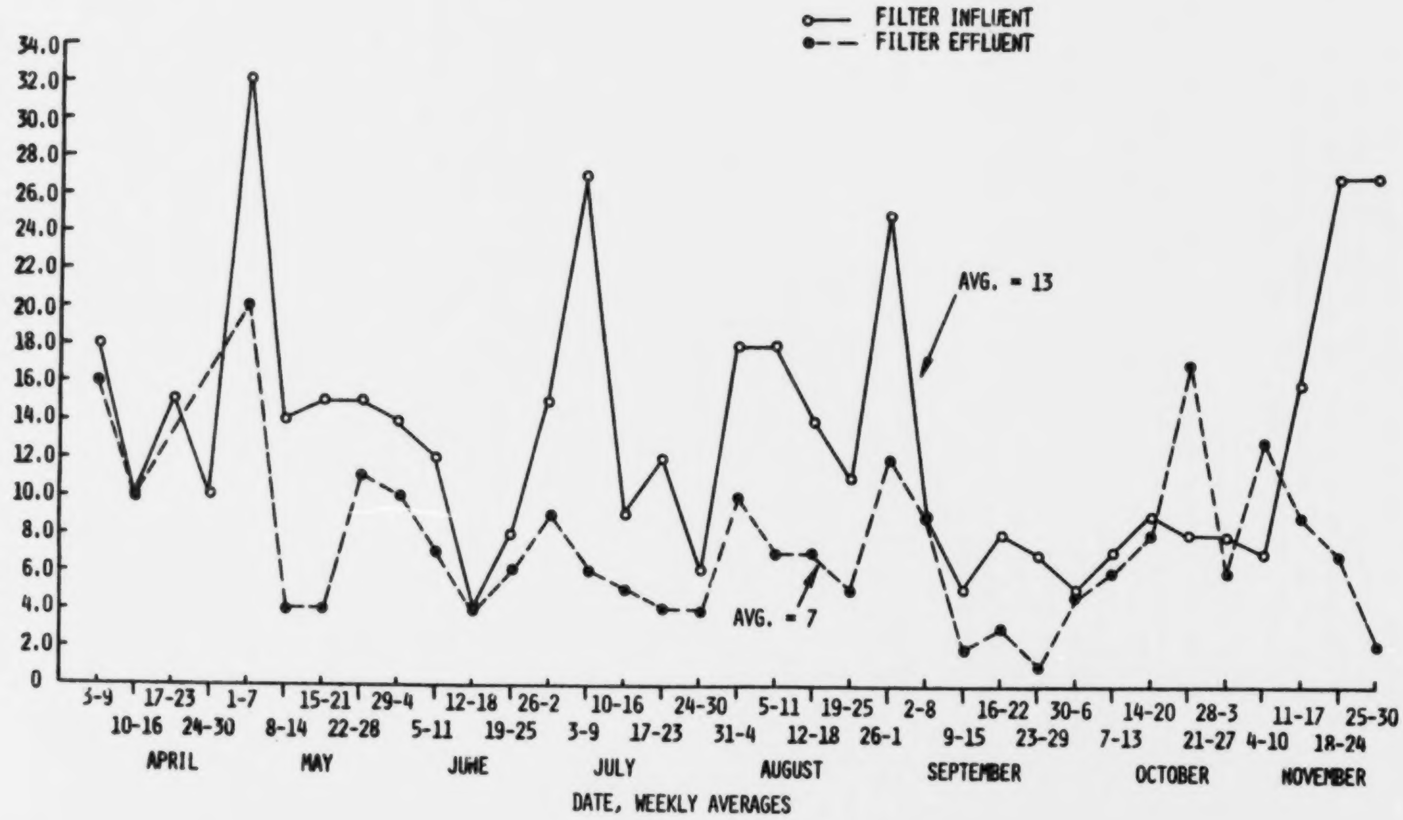


Figure 17. Mixed-media pressure filter suspended solids removal data.

higher than this due to the suspended solids that may have been produced in the carbon beds but not measured in the feed. Filter run times between backwashes were approximately 8 hours. A maximum feed concentration of 35 mg/l SS and an average effluent of 7 mg/l with an 8-hour run time corresponds to a filter loading of 3.4 Kg/m^3 (0.21 lbs/ft^3) of filter media.

Waste Sludge and Backwashes--

Grab samples of waste secondary sludge and backwashes from the sedimentation/filtration unit, carbon columns and multimedia filter were taken periodically and analyzed for COD, solids and heavy metals. A summary of this data is shown in Table 7 with more detailed data in Table 1 of Appendix B. These analyses refer to the concentration of materials in the original sample. They may be expressed as percent of dry solids by dividing the concentration of the metal ion by the total suspended solids and multiplying by 100.

The relatively high levels of calcium, magnesium and sodium result from the seawater based cooling-water system. Copper and iron levels result in part from material corrosion. The primary clarification system has pH adjustment for the precipitation of aluminum hydroxide. Incomplete removals in the primary clarifiers account for the presence of aluminum in the waste secondary sludge as well as the backwash waters. No traces of the toxic metals cadmium, mercury or arsenic were found in any of the samples.

Reverse Osmosis--

Tubular cellulose acetate--Operation began in April and continued until July 9, 1976 with the tubular cellulose acetate (CA) membranes. RO performance is summarized in Table 8 which shows averages taken over the entire test period. From the very beginning, poor conductivity rejection was experienced and averaged from a low of 67 percent to a high of 88 percent rejection, reducing the conductivity to approximately 1000 umho. Total dissolved solids rejection ranged from 73 to 97 percent (Table 2, Appendix B). These rejections were well below that stated by the manufacturer of these membranes. Conductivity in the range of 200 to 400 umho was required for satisfactory life of the downstream ion-exchange resin beds.

Several attempts were made to improve rejections by changing operating conditions of pH, temperature and pressure with negligible improvements. The manufacturer upon disassembling a module and analyzing the membranes concluded that the membranes had been damaged due to excessive heat and/or pH conditions outside the acceptable range. Heat damage most probably resulted from exposure to the sun, accounting for the poor rejections from the start.

TABLE 7. WASTE SLUDGE CHARACTERIZATION SUMMARY, OVERALL AVERAGES

Assay mg/l (Detectable Limit)	Waste Secondary Sludge	Sedimentation/ Filtration Unit Backwash	Multi-Media Filter	Carbon Column Backwash
pH	7.9	8.4	8.5	8.5
COD	14241	272	74	550
TSS	14468	303	11	161
TDS	3491	3465	2988	3485
Ca	138	58	53	53
Li (1.0)	Nil	Nil	Nil	Nil
Mg	49	5.9	4.7	5.4
K (0.1)	83	5.0	0.9	0.9
Na	1217	1088	1056	1212
Cd (1.0)	Nil	Nil	Nil	Nil
CrO_4	0.4	< 0.1	Nil	Nil
Cu (0.1)	0.7	0.1	< 0.1	Nil
Fe	24	2.3	0.7	5.2
Mn (0.1)	0.6	< 0.1	Nil	Nil
Al	130	5.9	1.2	2.4
Ni (0.1)	0.4	< 0.1	Nil	Nil
Zn (0.1)	2.7	0.15	0.1	0.1
Hg (0.05)	Nil	Nil	Nil	Nil
As (0.1)	Nil	Nil	Nil	Nil
SiO_2 (Si)	(48)	2.2	1.2	2.6

TABLE 8. REVERSE OSMOSIS DATA SUMMARY, OVERALL AVERAGES

Assay	Tubular Cellulose Acetate		Spiral-wound Cellulose Acetate		Spiral-wound Polyamide	
	Feed	Perm	Feed	Perm	Feed	Perm
pH	8.3	6.8	8.1	5.8	8.1	7.1
Conductivity, umho	5148	1086	4257	498	5858	477
Hardness, $CaCO_3$	61	9	66	8.5	53	0.7
Fe	0.43	0.35	0.54	0.41	0.29	0.14
TSS	14.7	12.2	8.4	0.58	11.9	1.7
TDS	3665	609	2924	313	4490	334
(TOC) COD	(48)	(14)	44.5	10	47	4
Silica, Si	8.3	4.7	11.4	3.9	6.6	1.9
Chloride	-	-	97.7	29.5	241	51

The test period using the tubular CA membranes was plagued with additional problems including rapid temperature buildup of the circulating water, faulty pH control, leaky brine seals and pump failures. One 30-day cooling-water test was conducted using RO product water produced by the tubular CA system and is not considered representative of RO performance. No boiler tests were conducted using renovated water produced during this time period.

At the manufacturer's recommendations, spiral-wound CA membranes were installed to replace the tubular CA membranes.

Spiral-wound cellulose acetate--The tubular CA membranes were replaced on July 10, 1976 with spiral-wound CA membranes. These membranes were selected primarily because of their much lower replacement cost than the tubular configuration for the same membrane surface area, and the fact that suspended solids were felt at this time to be low enough not to present a fouling problem in the spiral-wound configuration which has very small liquid flow channels.

The spiral-wound CA membranes performed very well during the first two weeks of operation, averaging greater than 95 percent dissolved solids rejection and approximately 70 percent COD rejection at 80 percent water recovery (Table 8 and Table 2, Appendix B). These removals were greatly improved over the previous tubular CA operation. However, after this initial period of operation, rejections decreased to the 85 percent level. Permeate flow also began to decline. Membrane fouling became apparent when the recommended cleaning solutions failed to improve rejections and permeate flow. Organic rejections (COD) varied between 55 and 100 percent during the period of operation using the spiral-wound CA membranes.

Several weeks of operation continued with many attempts to improve rejections and determine the cause of the membrane fouling. Upon acidifying the feed with sulfuric acid a clear gel-like substance was noted to frequently form in the feed tank at a $pH < 5.5$, but not above this pH. Although originally thought to be a silica precipitate, this was not confirmed. The precipitation of any materials in the RO unit must be avoided in any case to prevent membrane fouling. Disassembly and examination of one of the modules showed rust particles and a very fine black slime on the surface of the membrane. Because the cleaning solutions recommended for iron, heavy metals and organics were ineffective, particulates appeared to be the major cause of fouling.

A filter after the RO feed tank was originally thought not to be needed, since suspended solids were very low in the multimedia filter effluent; also the multimedia filter effluent was passed through a 10-micron cartridge filter before entering the RO feed tank. However, very fine particulates either passed through the filter or precipitated in the feed tank. Iron, resulting from corrosion of the carbon-steel feed tank, contributed solids to the RO feed-water.

In addition to membrane fouling, high circulating water temperature continued to be a problem. The rapid temperature buildup of the recirculating water appeared to be unavoidable in this batch-type process operation.

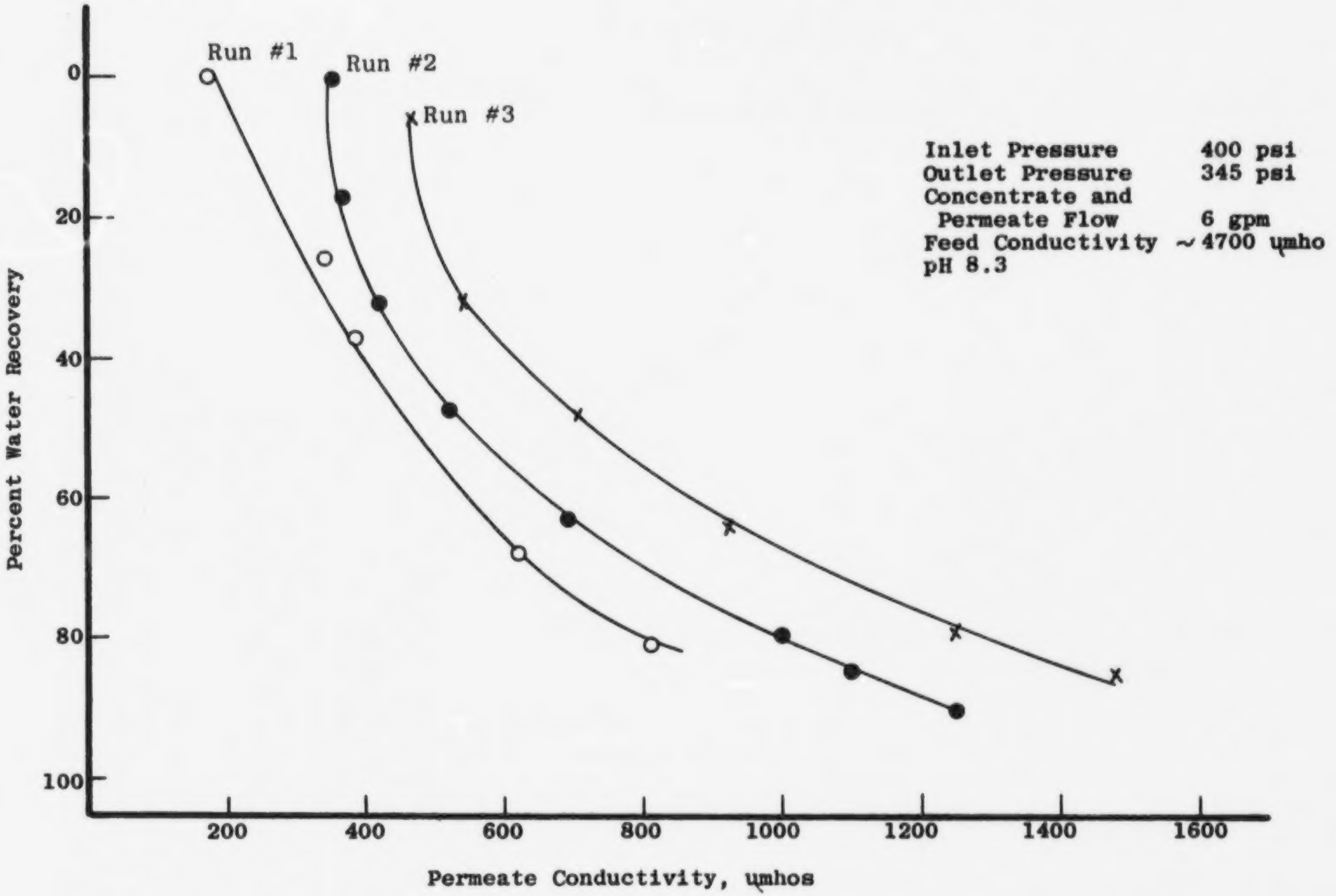
After 10 weeks of unsuccessful performance, polyamide spiral-wound membranes were installed. No cooling-water tests or boiler tests were conducted on water renovated using the spiral-wound CA membranes.

Spiral-wound polyamide--Spiral-wound polyamide (PA) membranes were placed in operation on October 7, 1976, based upon manufacturers' recommendation and their claims of the ability of these membranes to tolerate temperatures up to 27.2°C (135°F), pH ranges from 3 to 9, and greater organic rejections than the CA membranes. A 10-micron cartridge filter was installed between the RO feed tank and the RO pump suction as an additional precaution against suspended solids fouling the membranes.

The RO unit operated for seven consecutive weeks achieving consistently ~91 percent conductivity rejections. Organic rejections (COD) improved to an average 91.5 percent as well as near complete rejection of hardness (Table 8 and Table 2, Appendix B). Feed conductivity during this period ranged from 4000 to 9000 umho.

Rejections were found to decline with each consecutive batch run as shown in Figure 18. Increased fouling resulted in higher initial permeate conductivity as well as a more rapid increase in permeate conductivity as the batch became more concentrated. Ideally one would like these curves to be very steep with a sharp break at some higher percent water recovery. In all tests conducted, permeate conductivity increased rapidly at water recoveries beyond approximately 60 to 70 percent.

Test runs were conducted to determine if pH adjustment significantly affected conductivity rejection (Figure 19). It was found that by reducing the RO feed to pH ~5 that lower permeate conductivities were achieved with higher water recoveries before breakthrough of conductivity. This improvement



Inlet Pressure 400 psi
Outlet Pressure 345 psi
Concentrate and Permeate Flow 6 gpm
Feed Conductivity ~4700 umho
pH 8.3

Figure 18. Consecutive RO batch runs with spiral-wound PA membranes, 10/7/76.

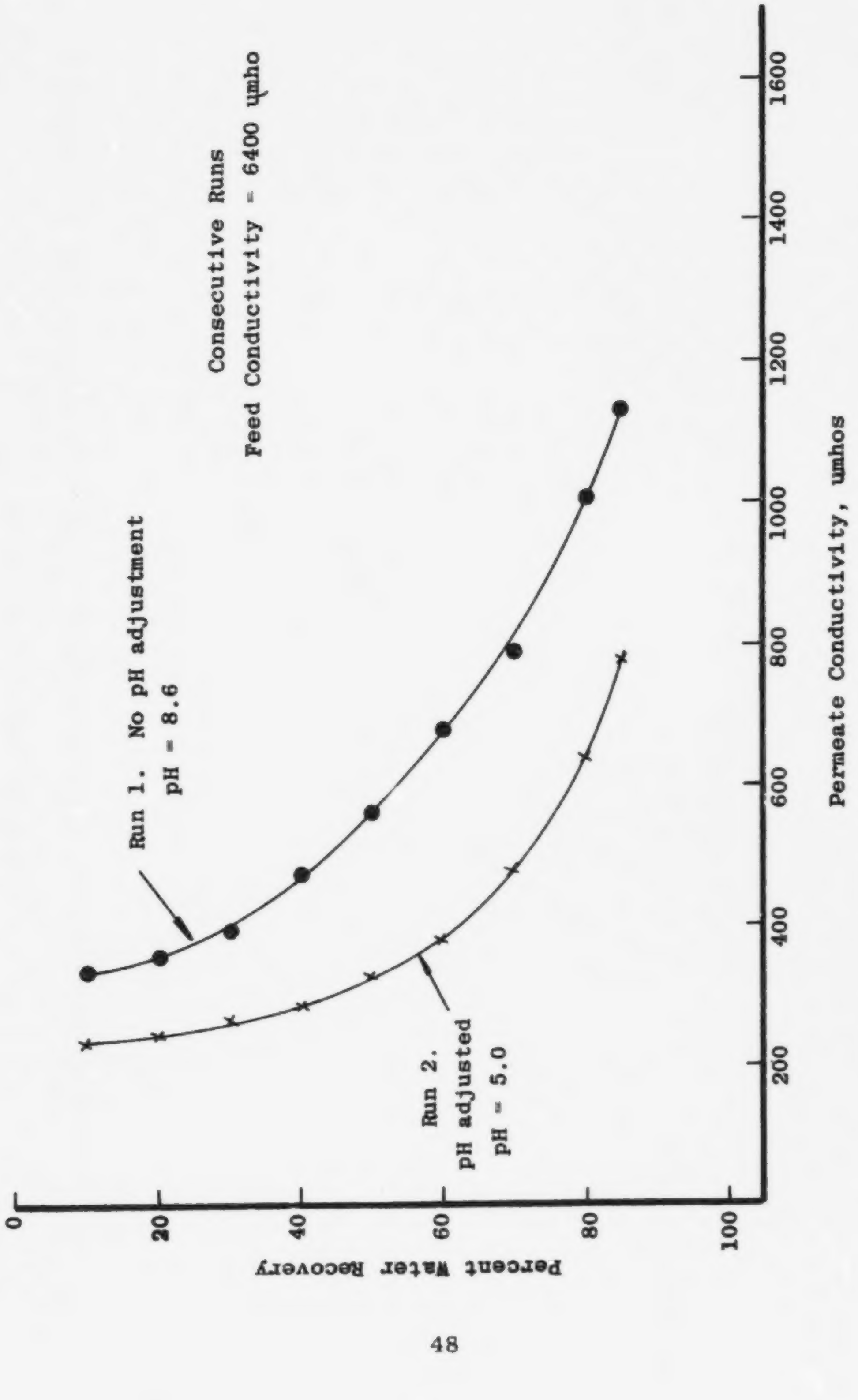


Figure 19. Effect of pH on conductivity rejection, 12/18/77.

with reduced pH was observed several times; however, upon reduction of the feed pH, more rapid plugging of the 10-micron filter between the feed tank and RO pump suction occurred. In all runs at the reduced pH, this filter was coated with the gel-like material previously addressed. The increase in the precipitation of salts at lower pH conditions and the resulting increase in filter plugging, or membrane fouling, must be weighed against the benefit of increased salt rejections. This fact could play a significant role in the cost effectiveness of reverse osmosis.

Although the use of the membrane cleaning solutions often proved ineffective in restoring salt rejection, it was observed several times that simply rinsing the membranes with demineralized water and letting them soak in demineralized water for a long period (1-2 weeks) restored the membranes' ability to reject dissolved salts and increased permeate flux to original levels. This phenomenon suggests that the membranes are not irreversibly fouled and that a more rapid cleaning procedure is needed. This observation was discussed with the RO manufacturer who indicated that this has been observed elsewhere, but as of yet is an unresolved problem.

Samples were taken periodically of the RO feed and permeate for more specific inorganic analyses (Tables 9 and 10). These values were utilized to insure the correct sizing of the RO unit in the full-scale design. Calcium, magnesium, sodium, bicarbonate, sulfate and chloride are the primary ions to be rejected. Sodium and chloride are among the ions most poorly rejected. The divalent ions were all rejected very well and would appear to present no problems in a full-scale unit.

Ion-Exchange--

The ion-exchange resin beds were operated only when needed to produce renovated water for feed to the pilot boiler. The ion-exchange unit was operated as a complete removal system such that when the effluent reached unacceptable quality, the beds were regenerated. The object was not to evaluate ion-exchange but to produce water satisfactory for feed to the boiler. Data collected routinely during operation is tabulated as weekly averages in Table 3, Appendix B and summarized in Table II. The average analyses over the entire study period indicated limited effectiveness of the primary deionizer (weak base anion) in scavenging the low concentrations of organics present. At these very low COD levels, which are at the very lowest limits of the analytical test, it is difficult to evaluate the resin's effectiveness in scavenging organics based upon COD alone.

TABLE 9. INORGANIC ANALYSIS FOR DESIGN OF DEMINERALIZATION SYSTEM

	Multi-Media Filter Effluent (R.O. Feedwater)												
Assay mg/l	Dates												
	8/24	8/26	8/31	9/2	9/7	9/9	9/16	9/21	10/1	10/9	10/24	11/2	Avg
pH	8.4	8.4	8.4	8.6	8.4	8.3	7.9	8.0	8.4	8.4	8.6	8.7	8.4
COD	41	34	12	45	40	55	-	-	-	20	-	-	30
Conductivity(umho)	4125	4625	2500	3250	4375	3625	4000	1375	4750	4437	5437	6625	4069
TDS	3318	3244	1998	2150	2650	2525	2336	883	3402	3326	4720	3910	2872
Total Hardness($CaCO_3$)	38	34	126	56	36	24	40	150	30	36	38	62	56
Alkalinity($CaCO_3$).P	68	84	70	100	80	12	34	22	84	100	144	104	75
M	1402	1598	1158	1360	1356	1134	576	308	1180	1184	2260	1224	1228
SiO_2(Si)	(12.0)	(17.0)	(14.3)	(11.5)	(9.0)	(8.0)	(2.6)	(13.0)	(8.6)	(6.3)	(8.0)	(5.0)	(9.6)
Fe	0.1	0.2	0.1	Nil	0.1	0.2	1.1	0.1	Nil	0.2	0.5	Nil	0.2
Mn	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Ca	3.6	2.3	35.8	5.1	3.0	4.9	4.4	4.8	3.0	3.2	2.1	1.7	9.7
Mg	40	42	8.2	4.5	3.3	4.0	1.9	10.0	4.2	5.0	5.0	92.8	18.3
Na	847	1128	634	828	1210	1012	752	250	1250	1150	1800	1707	1047
K	0.7	0.6	1.2	1.8	0.9	0.6	0.9	1.0	0.9	1.4	3.0	7.9	1.7
OH	0	0	0	0	0	0	0	0	0	0	0	0	0
CO_3	136	168	140	200	160	24	68	44	168	200	288	208	150
HCO_3	1266	1430	1018	1160	1196	1110	508	264	1012	984	1972	1016	1078
SO_4	350	452	252	242	1064	756	196	-	1600	829	952	448	649
Cl^-	96	182	71	62	75	62	57	36	20	112	136	388	108
NO_3	140	183	129	129	23	23	65	38	70	124	31	116	89
Ortho PO_4	9	35	15	18	70	35	40	6	25	-	20	7	25
Phenol	Nil	Nil	-	-	Nil	-	-	Nil	-	-	-	Nil	Nil

TABLE 10. INORGANIC ANALYSIS FOR DESIGN OF DEMINERALIZATION SYSTEM

Assay mg/l	Reverse Osmosis Permeate Dates 9/23	10/1	10/6	10/9	10/13	10/17	10/18	10/22	10/24	11/2	CA Avg	PA Avg
pH	5.7	6.6	6.9	7.5	6.6	8.3	7.7	7.5	8.0	7.6	6.4	7.6
Membrane	CA	CA	CA	PA	PA	PA	PA	PA	PA	PA	-	-
COD	-	-	16	16	20	24	29	-	-	24	16	23
Conductivity (umho)	179	488	456	613	431	450	500	550	631	890	374	580
TDS.	127	248	252	396	288	306	312	366	384	430	209	355
Total Hardness($CaCO_3$)	2	2	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	1.3	Nil
Alkalinity($CaCO_3$) P	0	0	0	0	0	8	0	0	0	0	0	1
M	20	24	52	104	66	130	134	154	180	120	32	115
SiO_2(Si)	1.0	2.9	2.5	1.6	1.1	1.3	1.3	1.0	1.0	1.3	2.1	1.2
Fe	Nil	0.1	0.3	Nil	0.1	Nil	Nil	Nil	Nil	Nil	0.1	Nil
Mn	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Ca	0.3	0.1	0.1	Nil	0.1	Nil	0.6	0.1	0.1	Nil	0.2	0.1
Mg	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	1.2	0.1	0.2
Na	20	86	90	127	92	95	119	156	187	244	65	146
K	Nil	0.1	0.1	0.1	0.3	Nil	0.1	0.1	Nil	0.8	<0.1	0.2
OH	0	0	0	0	0	0	0	0	0	0	0	0
CO_3	0	0	0	0	0	16	0	0	0	0	0	0
HCO_3	20	24	52	104	66	114	134	154	180	120	32	124
SO_4	7.2	3.4	3.4	3.4	3.4	5.6	11.8	16	27	10.1	4.6	10.0
Cl	2.0	101	43	46	55	34	24	30	50	141	49	54
NO_3	4.9	55	91	79	77	22	62	30	45	93	50	58
Ortho PO_4	1.0	3.0	Nil	Nil	Nil	1.0	Nil	2.0	Nil	Nil	1.3	0.4
Phenol	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

TABLE 11. ION-EXCHANGE DATA SUMMARY, OVERALL AVERAGES

Assay	RO Permeate	Primary Deionizer(1)	Secondary Deionizer(2)
pH	6.7	8.2	7.4
Conductivity, umho	516	418	5
Hardness, $CaCO_3$	9.0	9.4	1.3
Fe	0.25	0.13	0.12
TSS	1.0	1.0	0.0
COD	14	13	6
Silica, SiO_2	3.8	3.4	0.5
Chloride	33	23	1.8

(1) Weak-base anion exchange

(2) Mixed bed ion-exchange

Samples from the two ion-exchange columns were also taken periodically for more specific inorganic analysis that would enable an accurate sizing of full-scale demineralizers based upon the ions present in the water (Table 12). Primary leakage through the ion-exchangers was sulfate and chloride ions.

The on-line time for the pilot-scale exchangers ranged from 28 to 39 hours and averaged 35 hours before the secondary deionizer (mixed-bed) exhausted, requiring regeneration. Regeneration of the primary deionizer with caustic presented no problems. The secondary deionizer required an excessive amount of rinse water to clean the bed of regenerate. It was felt that this was due to poor flow distribution in the column which would cause excessive rinse requirements as a result of inadequate resin mixing. This fact, along with frequent shutdown of the reverse osmosis unit prevented a good water balance from being conducted on the pilot-plant facilities. A theoretical water balance based upon both the pilot-plant experiences and a continuous on-line demineralization system is presented and discussed under ESTIMATES OF INVESTMENT COST AND OPERATING EXPENSE FOR FULL-SCALE FACILITIES.

Demineralization Waste Brines--

In addition to the product water from the demineralization system waste streams are produced that contain a more concentrated solution of all the salts that were contained in the feedstream. These are the very salts that made the original feedstream unusable and, therefore, their disposal presents a serious and difficult problem. With a reverse osmosis system operated at 75 percent water recovery and the regeneration brines from the ion-exchange beds, the waste brine requiring disposal will be 30 percent or more of original wastewater flow entering the renovation facility.

Since the primary objective of these studies was the production of water for reuse in boilers, various alternatives for brine disposal were not evaluated, nor was the cost of disposing of these brines determined--a very important and significant factor in the overall cost of wastewater renovation.

Samples of the reverse osmosis brine as well as the ion-exchange regeneration brines were analyzed primarily for the various heavy-metals (Table 13). None of the very toxic metals (Hg, Cd, As) were found in concentrations above the detectable limit. The waste brines consist primarily of the measured ions sodium, calcium, magnesium, iron and aluminum and would contain as well significant levels of chloride, sulfate and bicarbonate. Although not reported here, the levels of these and other anions are easily estimated based upon their rejections and water recovery of the original feedstream.

TABLE 12. ION EXCHANGE INORGANIC ANALYSIS

	WB Organic Ion Exchanger Effluent								Mixed Bed Ion Exchanger Effluent							
	Dates								Dates							
Assay mg/1	10/1	10/2	10/13	10/16	10/18	10/22	10/24	Avg	10/1	10/2	10/13	10/16	10/22	10/24	11/2	Avg
pH	8.7	8.6	8.0	8.1	8.8	8.8	9.0	8.6	8.5	6.7	6.6	8.2	7.5	6.7	7.0	7.3
COD(TOC)	-	-	-	29	57	-	-	43	-	24	-	-	Nil	Nil	(3)	<8
Conductivity(umho)	412	419	418	456	331	456	631	446	4	2	4	3	3	1.5	0.9	2.6
Total Hardness($CaCO_3$)	4	Nil	Nil	6	Nil	Nil	Nil	1.4	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Alkalinity($CaCO_3$) P	8	12	4	64	4	18	30	20	0	0	0	0	0	0	0	0
.M	68	80	64	178	94	172	190	121	2	4	4	4	4	25	10	8
SiO_2	3.8	1.6	1.6	-	0.9	1.4	1.6	1.8	1.9	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Fe	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Mn	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Ca	0.2	0.1	0.1	0.1	0.3	0.1	0.2	0.2	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Mg	0.2	Nil	1.1	-	Nil	0.1	0.1	0.3	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Na	81	85	92	95	74	119	200	107	0.5	Nil	3.9	Nil	Nil	Nil	Nil	0.6
K	0.1	0.5	0.2	Nil	Nil	Nil	0.1	0.1	Nil	Nil	0.3	Nil	Nil	Nil	Nil	<0.1
OH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO_3	16	24	8	128	8	36	60	40	0	0	0	0	0	0	0	0
HCO_3	52	56	56	50	86	136	130	81	2	4	4	4	4	25	10	8
SO_4	14.0	23	3.5	6	12	17	37	16	1.2	5.6	3.4	Nil	11.2	Nil	1.1	3.2
Cl	Nil	29	41	38	14	29	36	27	24.0	2.9	3.9	3.0	10.0	1.0	10.0	7.8
NO_3	56	-	84	54	52	39	32	53	Nil	0.9	1.8	4.5	0.9	2.2	2.2	1.8
Ortho PO_4	3	Nil	Nil	1	Nil	3	Nil	1	15	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Phenol	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

TABLE 13. DEMINERALIZATION WASTE BRINE CHARACTERIZATION

Assay mg/l (Detectable Limit)	Reverse Osmosis Brine								Regeneration Brine WB Organic Ion Exchanger				Regeneration Brine Mixed Bed Ion Exchanger			
	Dates						CA Avg	PA Avg	Dates							
	9/22	10/4	10/9	10/16	10/22	10/24			9/18	10/14	10/23	Avg	9/18	10/15	10/23	Avg
Membrane	CA	CA	PA	PA	PA	PA										
% Recovery	80	80	80	80	80	80	80	80								
pH	7.3	7.2	8.3	8.2	8.8	8.6	7.2	8.5	11.7	12.2	12.2	12.0	--	11.3	1.6	6.5
COD	--	--	181	145	130	155	--	152	--	48	100	74	--	37	25	31
TSS	28	43	47	33	24	55	36	40	22	44	32	33	--	81	38	60
TDS	11164	14848	15772	12566	19743	13493	13006	18645	13325	18392 ,	9528	13748	--	15498	17003	16250
Ca	77	132	150	128	108	130	105	124	94	144	114	117	174	130	108	137
Li (1.0)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Mg	35	26	38	18.5	15.5	23.5	31	25	0.1	0.8	0.7	0.5	3.8	6.1	3.5	4.5
K	3.0	4.5	6.1	1.9	10.5	3.6	3.8	5.5	10.0	1.9	1.8	4.5	2.6	2.4	1.8	2.3
Na	3650	4860	5250	3780	3687	5250	4255	4491	8060	6330	4213	6201	3200	4268	3625	3697
Cd (1.0)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
CrO_4	0.1	Nil	Nil	Nil	Nil	0.1	<0.1	<0.1	0.1	Nil	Nil	<0.1	0.1	Nil	0.2	<0.1
Cu	0.2	0.1	Nil	Nil	0.1	0.2	0.15	<0.1	0.1	Nil	Nil	<0.1	0.1	Nil	0.1	<0.1
Fe	4.0	1.5	0.4	0.2	0.3	0.2	2.7	0.2	1.7	4.5	5.7	4.0	6.9	11.7	15.6	11.4
Mn	0.1	0.1	Nil	Nil	Nil	Nil	0.1	Nil	Nil	Nil	Nil	Nil	0.1	0.1	Nil	<0.1
Al	--	2.3	3.1	2.1	6.0	3.5	2.3	3.7	--	1.1	1.5	1.3	--	1.8	0.9	--
Ni	0.2	0.1	Nil	Nil	0.1	--	0.1	Nil	0.3	Nil	Nil	<0.1	0.3	Nil	0.1	<0.1
Zn	0.4	0.2	0.5	0.1	--	--	0.3	0.2	0.1	0.1	Nil	<0.1	0.3	0.4	--	0.3
Hg (0.05)	--	Nil	--	--	Nil	--	Nil	Nil	--	--	--	--	--	--	--	--
As (0.1)	--	Nil	--	--	Nil	--	Nil	Nil	--	--	--	--	--	--	--	--
SiO_2	--	2.3	4.2	3.5	3.5	3.6	2.3	3.4	--	1.0	1.0	1.0	--	4.1	3.0	3.6

At costal locations, an obvious method of disposal is through a seawater outfall. The dangers of high salt concentrations on the land are avoided and the effects of the brine discharge are minimal and localized as a result of re-dilution effects of runoff and river inflows. It is very possible to design an outfall system with the proper choice of diffuser that will control the initial dilution of the effluent to meet a predetermined acceptable level and thus minimize or avoid environmental problems.

Alternate methods of brine disposal include: solar evaporating ponds, deep-well injection, and concentration/mechanical drying followed by landfill of solids. Typical costs of disposal of waste brines using the various methods range from $1.00 to $10.00 per 1000 gallons of brine (5,6). At a given location, the geological and meterological conditions will determine which disposal method is most economical. For coastal locations, dispersion in an ocean outfall appears to be most economical. For inland facilities, solar evaporation offers an environmentally acceptable and economically reasonable disposal method--provided the evaporation rate exceeds the precipitation rate (primarily southwestern U.S.). For deep-well disposal suitable underground formations must exist, which is not the case in many areas. Mechanical drying requires high energy consumption and as a result has a very high cost (7,8,9).

Specific Organic Analyses--

Analyses for specific organic compounds were made on samples of wastewaters from the pilot-plant. The samples included: (1) sedimentation/filtration effluent, (2) carbon column effluent, (3) reverse osmosis effluent and (4) ion-exchange column effluent. Specific compound identification and quantification were made using a direct-inject gas chromatographic (GC) procedure which gave a limit of detection of ~1 mg/l. Additional specific compounds present in lower concentrations (parts per billion range) were identified but not quantified by a concentrating procedure followed by a gas chromatographic/mass spectrometric analyses.

Direct-inject GC analyses--The results of the direct-inject GC analyses are shown in Table 14. The direct-inject GC study included analyses for so-called "volatile" organics and glycols. The "volatile" materials are organics detectable by GC and include such compounds as ketones, esters, alcohols, aromatics and organic acids. Most of these compounds were detected using a 6.1-m (20-ft) column packed with CARBOWAX 20M on Chromosorb W; organic acids, however, required a column packed with Porapac Q which had been pre-treated with phosphoric acid. Glycols were analyzed by preparing a trimethylsilyl derivative followed by GC determination. These procedures are described in Appendix A.

TABLE 14. SPECIFIC COMPOUNDS ANALYSES - DIRECT-INJECT

Compound	Sedimentation/ Filtration Effluent, mg/l (a)	Carbon Column Effluent, mg/l	RO Effluent, mg/l	Ion Exchange Effluent, mg/l
Acetone	<1	-	-	-
Methyl ethyl ketone	<1	-	-	-
Toluene	5	-	-	-
Isobutanol	~1	-	-	-
Ethyl benzene	<1	-	-	-
n-Butanol	~1	-	-	-
Cumene	<1	-	-	-
Styrene	<1	-	-	-
Acetophonone	5	-	-	-
Naphthalene	~1	-	-	-
Phenol	<1	-	-	-
Acetic acid	44	24	(b)	-
Propionic acid	42	8		-
Isobutyric acid	2	2		-
Butyric acid	13	5		-
Ethylene glycol	12	5	(b)	trace
Propylene glycol	-	-		-
Diethylene glycol	3	-		-
Ethoxytriglycol	-	-		-
Triethylene glycol	5	-		-

(a) Materials indicated at <1 mg/l were present in the biological feed but below quantifiable levels in the effluent.

(b) RO effluent not analyzed for organic acids or glycols.

In the analyses, twenty specific compounds were identified and quantified in the feed to the biological system. In general, the major components were glycols, organic acids, alcohols, ketones and aromatic products of the olefins operation. All of these compounds were reduced significantly or not detected in the biological effluent (sedimentation/filtration effluent) indicating excellent removal of these specific compounds by biological treatment.

Specific compounds were not detected by direct-inject GC using the CARBOWAX 20M column in samples of the carbon column effluent, RO effluent and ion-exchange effluent. These results indicate that if such specific compounds were present, they were in concentrations less than the detectable limits of the method (< 1 mg/l). Using the acid-treated Porapac Q column, small amounts of organic acids were found in the carbon column effluent but were not detected in the ion-exchange effluent, probably having been adsorbed in the weakly-basic ion-exchange bed. A small amount of ethylene glycol was indicated in the carbon column effluent with only a trace (< 1 mg/l) being found in the ion-exchange effluent. These results show that specific compounds, if present in the ion-exchange effluent, are in parts per billion concentrations and not detectable by direct-inject GC analyses.

Additional specific compound identification--Additional specific compounds were identified by concentrating the contained organics in the samples followed by GC-mass spectrometer identification. The analyses were made to identify compounds present in very low concentrations and not detected in the direct-inject GC procedures. These specific compounds were not quantified because of the relatively large amount of work involved. The concentrating procedure employed methylene chloride in several extractions and is described in Appendix A. The contained organics in the samples were concentrated at least a thousand-fold in the operation and thus were contained in the starting water samples in the parts per billion range or less. Organic acids would be detected in the procedure; glycols probably would not.

Seven additional specific compounds were identified in the effluent from the biological system (sedimentation/filtration effluent). These compounds as well as those detected in the carbon column effluent, RO effluent and ion-exchange effluent are listed in Table 15. Toluene was found in the carbon column effluent but not in the preceding sedimentation/filtration unit effluent. Both the RO and ion-exchange effluents contained only formamide, xylene and ethyl benzene. The presence of formamide probably resulted from the use of formaldehyde in the RO membrane cleaning solution for the control of bacterial growth.

TABLE 15. ADDITIONAL SPECIFIC COMPOUNDS DETECTED IN PONCE WATER REUSE SAMPLES[a]

Sedimentation/Filtration Effluent	Carbon Column Effluent	RO Effluent	Ion Exchange Column Effluent
Acetone	Acetone	Formamide	Formamide
Ethyl benzene	Toluene	Xylene	Xylene
Xylene	Ethyl benzene	Ethyl benzene	Ethyl benzene
Styrene	Xylene		
$C_{10}H_{14}$aromatic			
Methyl styrene			
$C_{10}H_{20}$			

(a) These compounds contained in ppb range or less.

After treatment with activated carbon, no specific compounds were detected by direct injection in the GC analysis using the CARBOWAX 20M column. After complete treatment through the renovation facilities, the resulting water for feed to the pilot boiler contained only trace amounts (ppb) of formamide, xylene, ethyl benzene and ethylene glycol.

INVESTMENT COST AND OPERATING EXPENSE FOR FULL-SCALE FACILITIES

This section presents estimates of fixed investment and operating expenses for a full-scale tertiary treatment system, very similar to the pilot-plant, which could produce renovated wastewater suitable primarily for boiler feedwater. Because of the very unique characteristics of each chemical plant's wastewater these economic data should not be construed to reflect cost and expenses from an optimum-designed wastewater renovation facility suited for petrochemical plants in general, but rather as a basis from which reasonable economic data can be extrapolated for specific situations.

These data were developed by the Cost Estimating Section of UCC's Engineering Department and approach the quality of estimates used for major capital budget requests. Two design cases were estimated having wastewater flow as their only difference. This hypothetical facility shown in a conceptual layout in Figure 20 is proposed for UCCI's organic chemical manufacturing complex near Ponce, Puerto Rico.

The following general specifications and assumptions were the basis for developing these costs and expenses:

- The influent to the tertiary treatment facility is UCCI plant's wastewater after primary and secondary (activated sludge) treatment. Two design cases will be considered: Case A--5.7 m^3/min (1500 gpm) and Case B--11.4 m^3/min (3,000 gpm). The renovated water is to be used as boiler feedwater for 1100 psig, 750°F steam. Average water recovery is 67 percent.
- All backup and support facilities such as electrical power, steam, instrument air, roadways, etc., are available at the tertiary treatment facility battery limits and no additional general facilities are required. Also assume that waste sludge and brine disposal facilities are existing and no additional costs or expenses will be incurred.

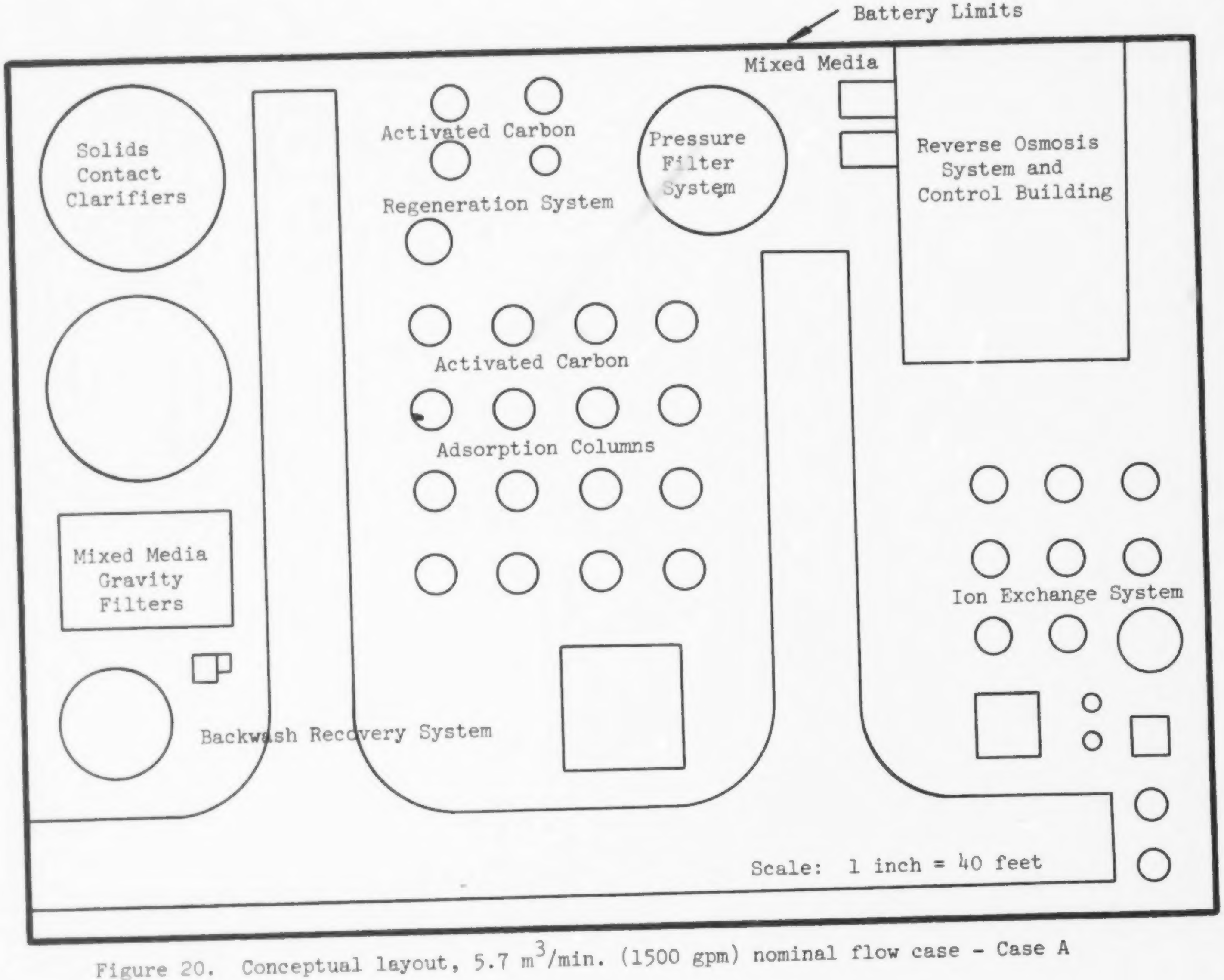

Battery Limits
Mixed Media
Solids Contact Clarifiers
Activated Carbon Regeneration System
Pressure Filter System
Reverse Osmosis System and Control Building
Activated Carbon Adsorption Columns
Mixed Media Gravity Filters
Ion Exchange System
Backwash Recovery System
Scale: 1 inch = 40 feet

Figure 20. Conceptual layout, 5.7 m^3/min. (1500 gpm) nominal flow case - Case A

- Fixed investment costs are based upon fourth quarter 1978 mechanical completion. Direct and period operating expenses are 1979 dollars that do not include depreciation. No credit is taken for any tertiary treatment investment cost or operating expenses that might be required as a result of more stringent effluent guidelines resulting in some part or all of the tertiary treatment effluent being disposed of in some receiving body of water.

Process Description

With the exception of the sedimentation/filtration unit the estimated full-scale facility's process and equipment very closely parallel that of the pilot-plant. In the early phases of the experimental program it became apparent that the biological system's residual suspended solids were readily removed in the sedimentation/filtration step, thus a more conventional reactor clarifier was used for solids removal in this full-scale projection.

The clarified secondary effluent would flow into two solids contact clarifiers where polyelectrolyte would be added. This clarifier overflow would flow by gravity through three multimedia filters operated in parallel. The filtered water would be pumped from a clearwell into the activated carbon adsorption columns arranged in four parallel lines of three adsorbers in series with one standby adsorber. Spent activated carbon would be regenerated on site in a multiple-hearth furnace. Carbon column effluent would be filtered in two parallel multi-media pressure filters and pumped to a reverse osmosis system. Demineralization of the reverse osmosis permeate would be completed by ion exchange. Portions of the ion exchange regeneration cycle rinse water would be recycled to the reverse osmosis system. Spent backwash from the gravity filters, pressure filters and carbon columns, flows to a flocculation tank where a polyelectrolyte would be added. The flocculated backwash would then be clarified and recycled to the secondary treatment system.

Due to equipment limitations, direct scaleup from pilot-scale to full-scale is not always possible. A water balance estimated for a wastewater flow of 5.7 m^3/min (1500 gpm) based upon pilot-scale experience and sizing of full-scale facilities indicates a maximum achievable water recovery of 67 percent (Figure 21). The remaining water is contained in waste sludge and brines that would require disposal. Approximately the same percent of water recovery would be realized through a system treating 11.4 m^3/min (3000 gpm). Higher waste loads or more

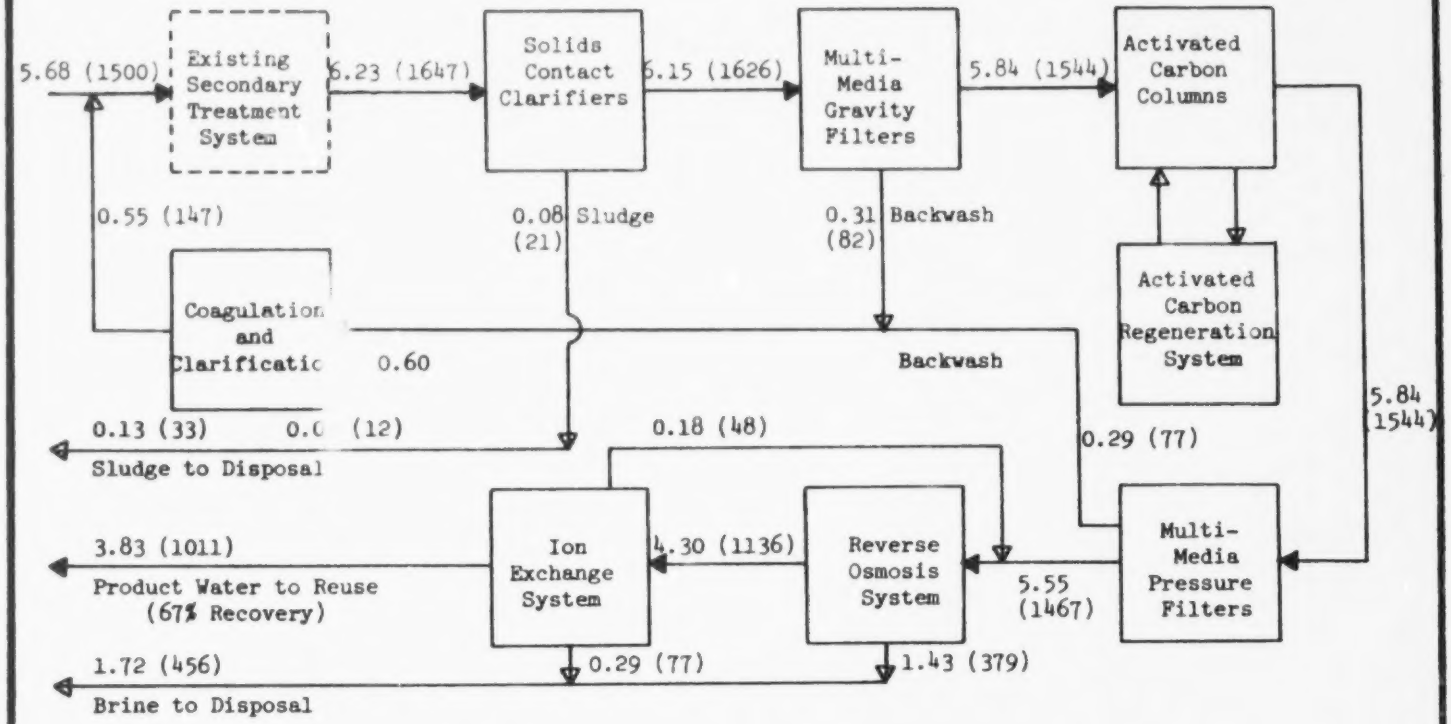

5.68 (1500)
Existing Secondary Treatment System
6.23 (1647)
Solids Contact Clarifiers
6.15 (1626)
Multi-Media Gravity Filters
5.84 (1544)
Activated Carbon Columns
Activated Carbon Regeneration System
0.55 (147)
0.08 (21) Sludge
0.31 (82) Backwash
Coagulation and Clarificatic
0.60
Backwash
5.84 (1544)
0.13 (33)
0.0 (12)
Sludge to Disposal
0.18 (48)
0.29 (77)
3.83 (1011)
Product Water to Reuse (67% Recovery)
Ion Exchange System
4.30 (1136)
Reverse Osmosis System
5.55 (1467)
Multi-Media Pressure Filters
1.72 (456)
Brine to Disposal
0.29 (77)
1.43 (379)

Figure 21. Wastewater renovation plant schematic diagram.
5.7 m^3/min (1500 gpm) Nominal Flow Case
Average flow rates are in m^3/min. (gal./min)

variable streams would significantly affect the water balance, yielding decreased water recoveries, due to increased sludge/brine residues. Water recovery is strongly dependent upon the blowdown, regeneration, backwash and cleaning requirements of each unit operation. Because these streams are unavoidable, complete water reuse becomes increasingly more difficult to achieve with higher qualities of water required for reuse.

How the projected full-scale wastewater renovation facilities were sized, along with differences from the pilot facilities tested is summarized in Appendix C. References 10 through 20 listed in the Bibliography were utilized for the sizing and cost estimation of full-scale facilities.

Summary of Economics

Fixed investment and annual operating costs for each treatment step are broken down in Table 16. Total costs and miscellaneous usage rates for the full-scale facilities are summarized in Table 17.

The total annualized cost of producing water of boiler feedwater quality through this tertiary renovation sequence would be approximately \$2.00/m^3 (\$7.50/1000 gallons) in 1978. This does not include any primary or secondary treatment costs; nor does it include facilities for the handling and disposal of waste brines and sludges. The disposal of these waste streams is expected to be high with little to no additional water recovered.

Carbon adsorption and carbon regeneration facilities make up approximately 35 percent of the total fixed investment and greater than 30 percent of the total annual operating expense. Reverse osmosis accounts for an additional 25 percent of the total fixed investment and 30 percent of the annual operating expense. A water reuse facility using these treatment steps will require reductions in the cost of carbon adsorption and/or reverse osmosis to significantly improve the sequences' cost effectiveness. Lesser quality waters for use in low pressure steam systems or as cycle cooling-water can be obtained at significantly lower cost.

TABLE 16. INVESTMENT AND OPERATING COST SUMMARY

THOUSANDS OF DOLLARS

CASE A: Plant Influent Rate; 5.7 m^3/min (1,500 gpm)

CASE B: Plant Influent Rate; 14.4 m^3/min (3,000 gpm)

	Suspended Solids Removal		Activated Carbon		Carbon Regeneration		Pressure Filtration		Reverse Osmosis		Ion Exchange		Backwash Recovery		Total	
Fixed Investment	Case A	Case B	Case A	Case B	Case A	Case B	Case A	Case B	Case A	Case B	Case A	Case B	Case A	Case B	Case A	Case B
Material and Equipment	694	966	1813	3195	941	1012	423	673	2293	4457	1439	2249	140	193	7,743	12,745
Construction Labor	380	471	450	813	124	124	150	253	140	224	250	386	111	153	1,614	2,424
Construction Overhead(4)	331	412	411	727	115	116	133	223	143	236	228	353	96	132	1,457	2,199
Engineering and Startup	476	628	910	1605	400	424	239	390	873	1667	649	1013	118	162	3,665	5,889
Contingencies(5)	470	619	898	1585	395	419	236	385	863	1646	641	1000	116	160	3,619	5,814
Total Fixed Investment	2351	3096	4491	7925	1975	2095	1181	1924	4312	8230	3207	5001	581	800	18,098	29,071
Annual Operating Costs																
Utilities	4	6	21	44	10	17	1	2	190(1)	380(1)	80(1)	160(1)	1	1	307	610
Chemical Flocculant	86	172	-	-	-	-	80	161	-	-	-	-	14	25	180	358
Furnace Fuel	-	-	-	-	38	71	-	-	-	-	-	-	-	-	38	71
Material Replacement	-	-	-	-	78(2)	157(2)	-	-	102(3)	204(3)	-	-	-	-	180	361
Operating Labor	30	30	30	30	122	122	30	30	49	49	49	49	-	-	310	310
Maintenance	143	189	274	483	121	128	72	117	263	502	196	305	35	49	1,104	1,773
Plant Overhead	47	80	20	29	95	141	43	75	131	244	50	80	6	10	392	659
Total Annual Operating Cost	310	477	345	586	464	636	226	385	735	1379	375	594	56	85	2,511	4,142

---

(1) Includes cost of utilities plus chemicals.

(2) Carbon replacement.

(3) Membrane replacement.

(4) Includes supervision, purchasing, accounting, warehousing, material control, temporary buildings and other indirect costs.

(5) Contingencies: 25% of engineering, equipment, and construction cost.

TABLE 17. TOTAL COSTS OF WASTEWATER RENOVATION FACILITIES

	Case A	Case B
Plant Influent Flow, m^3/min (gpm)	5.7 (1500)	11.4 (3000)
Boiler Feedwater Production, m^3/min (gpm)	3.8 (1010)	7.6 (2020)
Percent Water Recovery	66.7	66.7
Fixed Investment	$18,100,000	$29,100,000
Annual Operating Costs	$2,500,000	$4,100,000
Product Cost(1), \$/m^3 (\$/1000 gal.)	$2.00 ($7.50)	$1.60 ($6.05)
Miscellaneous Production and Usage Rates		
Additional Operators Required	13	13
Plant Area, m^2 (ft^2)	7,300 (78,000)	10,800 (116,000)
Utilities Usage:		
Electricity, KWH/yr.	7,700,000	15,000,000
Low-pressure steam, kg/yr (MM lbs/yr)	850,000 (1.9)	1,700,000 (3.7)
Instrument Air (2), m^3/yr (MM ft^3/yr)	425,000 (15)	425,000 (15)
Waste brine production, m^3/day (gpd)	2448 (662,400)	4896 (1,324,800)
Waste sludge production, (3) m^3/day (gpd)	187 (47,500)	374 (95,000)

(1) Based upon depreciation of fixed investment at 8 percent per year.

(2) Volume at 1 atmosphere pressure and 21°C.

(3) Based upon 0.5 percent solids.

SECTION 5

BOILER TEST LOOP

GENERAL FACILITY DESCRIPTION

The boiler test loop was designed by Betz Environmental Engineers, Inc. The carbon steel test boiler was similar to the research boilers built and operated by Betz Laboratories in their product evaluation studies. The entire boiler test loop was a skid-mounted package consisting of feed pumps, chemical addition facilities, deaerating heater, boiler, superheater, steam condensers, and sample coolers.

The boiler configuration and supporting facilities are illustrated in Figures 22, 23, and 24. Photographs of the boiler control panel and configuration of the boiler drums are shown in Figures 25 and 26, respectively.

Demineralized water from the boiler feedwater storage tank was pumped into the steam-heated deaerator where the bulk of the dissolved oxygen was driven off by heating the water to saturation. Hydrazine to remove the remaining oxygen and internal boiler water treatment chemicals to prevent scaling and fouling were added to the boiler feedwater as it left the deaerator.

The test boiler was a two-drum design similar in configuration to a standard "D" type industrial boiler with an external separator installed between the steam drum and the superheater to remove entrained water droplets. The boiler was designed to produce up to 81.7 Kg/hr (180 lbs/hr) of saturated steam at pressures up to 119.5 Kg/cm^2 (1700 psig). Heat input to the boiler was through electrical resistance heating elements. Boiler output and boiler heat flux were controlled by varying the size and rating of boiler heaters in service.

Saturated steam leaving the boiler passed through an electrically heated carbon steel superheater. Control of superheat temperature up to 399°C (750°F) was accomplished by varying the number of heating elements in service.

Steam from the superheater flowed to surface condensers. The steam condensate then passed through a corrosion test loop to monitor the effect of any contaminant on corrosion test coupons.

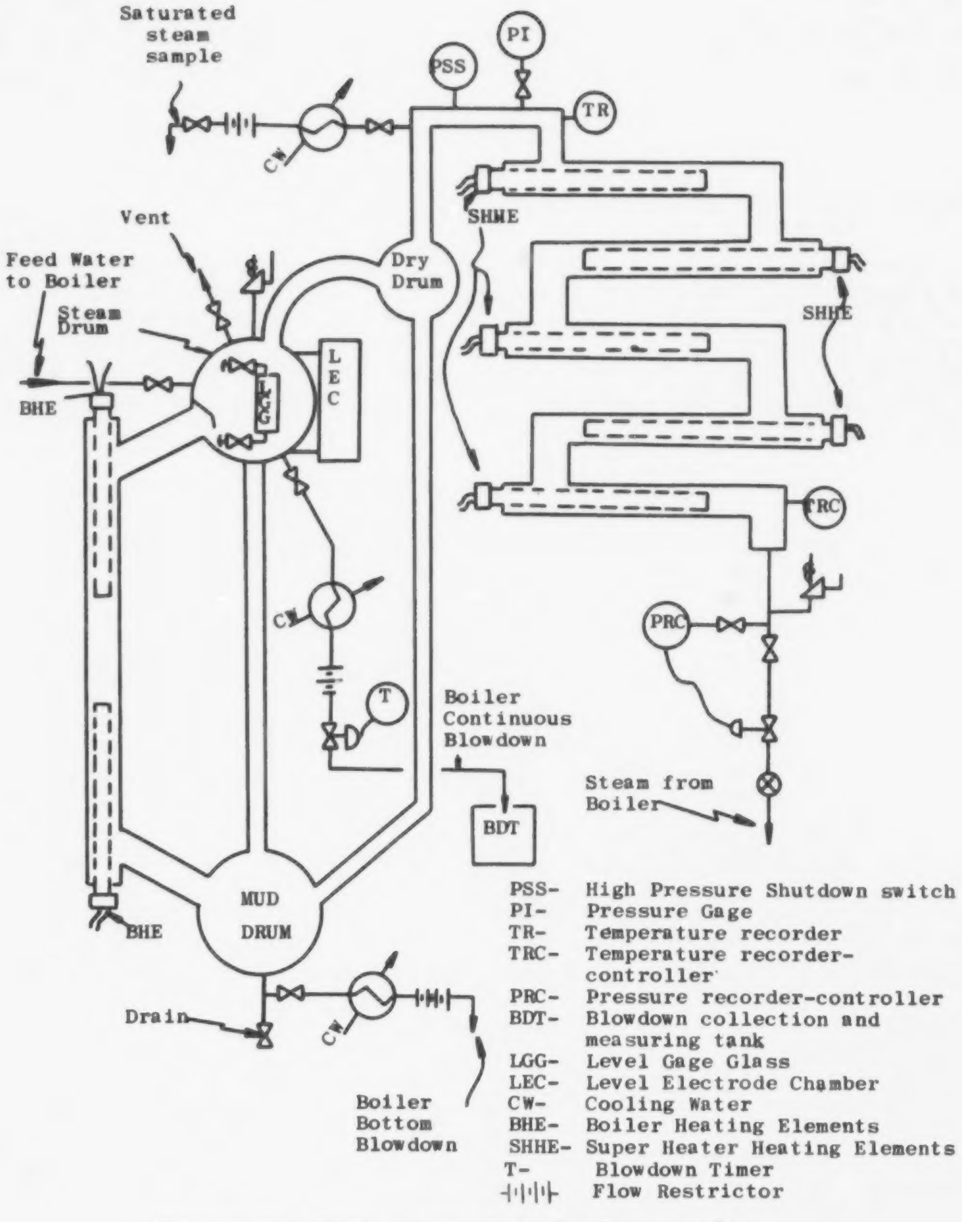

Saturated steam sample
PSS
PI
TR
CW
Vent
Feed Water to Boiler
Steam Drum
BHE
SHHE
Dry Drum
L E C
LGG
SHHE
TRC
PRC
CW
T
Boiler Continuous Blowdown
BDT
Steam from Boiler
MUD DRUM
BHE
Drain
CW
Boiler Bottom Blowdown
PSS- High Pressure Shutdown switch
PI- Pressure Gage
TR- Temperature recorder
TRC- Temperature recorder-controller
PRC- Pressure recorder-controller
BDT- Blowdown collection and measuring tank
LGG- Level Gage Glass
LEC- Level Electrode Chamber
CW- Cooling Water
BHE- Boiler Heating Elements
SHHE- Super Heater Heating Elements
T- Blowdown Timer
-|·|·|·|- Flow Restrictor

Figure 22. Boiler test-loop boiler section.

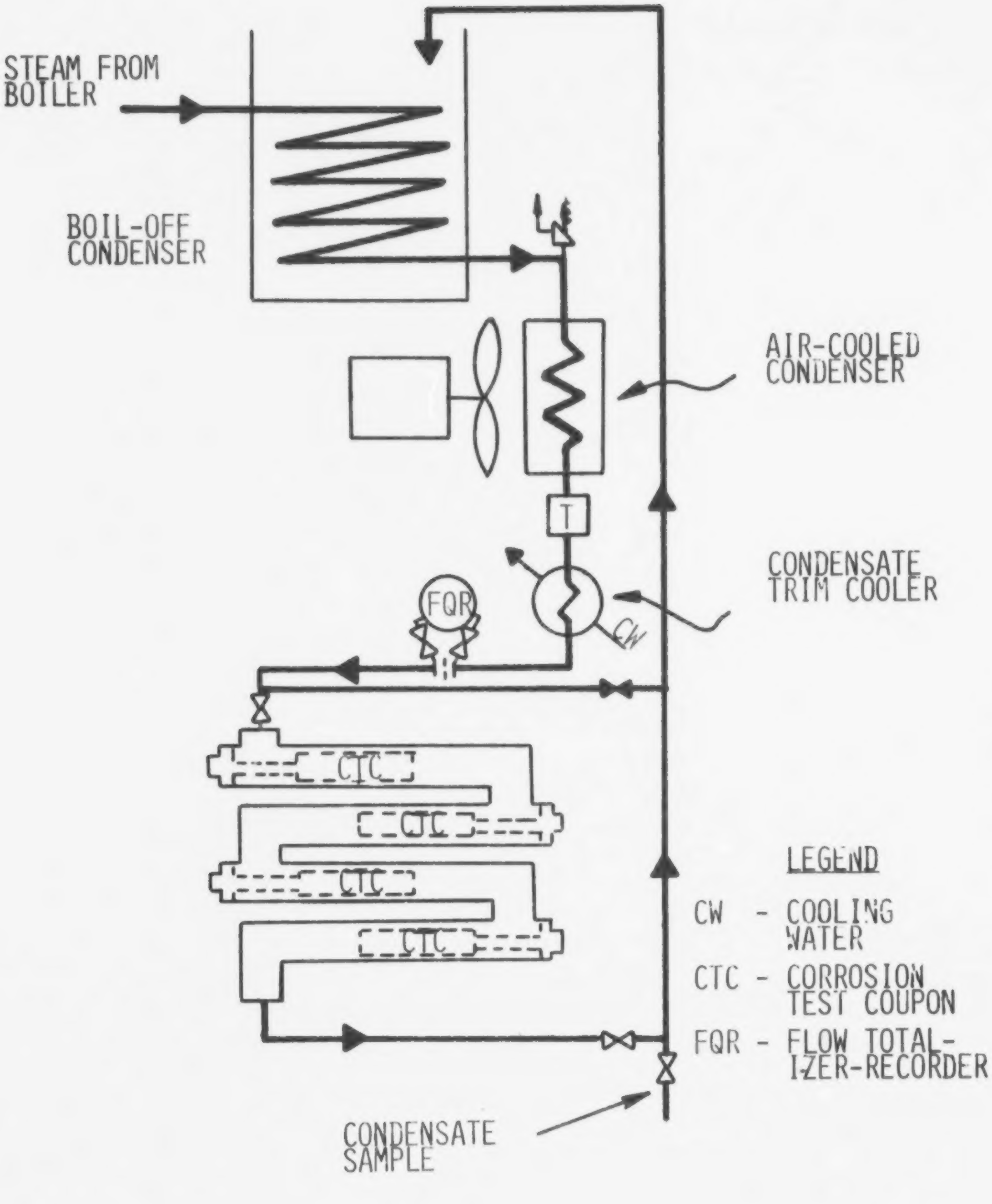

STEAM FROM BOILER
BOIL-OFF CONDENSER
AIR-COOLED CONDENSER
T
CONDENSATE TRIM COOLER
FQR
CW
CTC
CTC
CTC
CTC
LEGEND
CW - COOLING WATER
CTC - CORROSION TEST COUPON
FQR - FLOW TOTALIZER-RECORDER
CONDENSATE SAMPLE

Figure 23. Boiler test-loop condenser section.

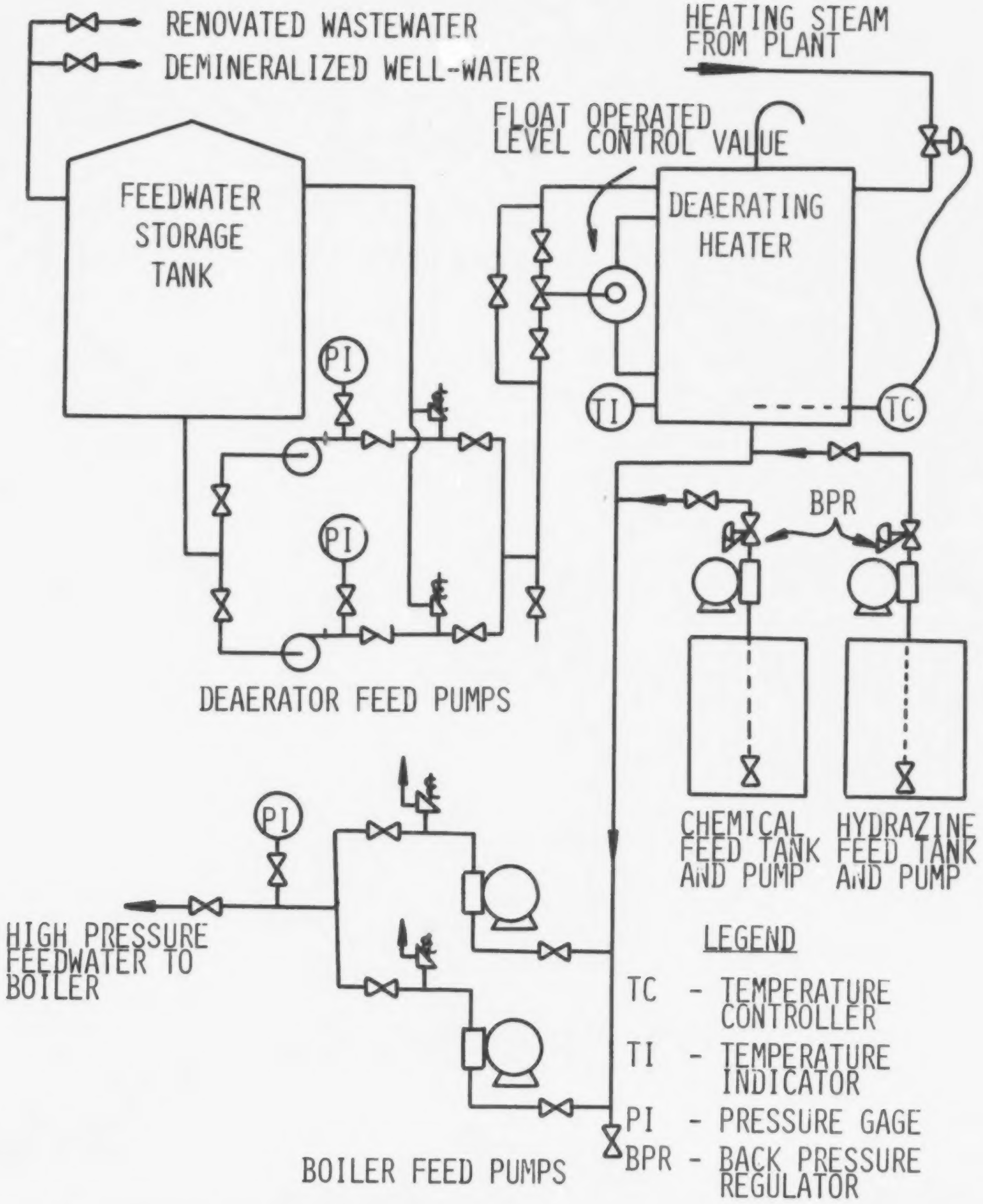

RENOVATED WASTEWATER
DEMINERALIZED WELL-WATER
HEATING STEAM FROM PLANT
FLOAT OPERATED LEVEL CONTROL VALUE
FEEDWATER STORAGE TANK
DEAERATING HEATER
PI
PI
TI
TC
BPR
DEAERATOR FEED PUMPS
CHEMICAL FEED TANK AND PUMP
HYDRAZINE FEED TANK AND PUMP
PI
HIGH PRESSURE FEEDWATER TO BOILER
BOILER FEED PUMPS
LEGEND
TC - TEMPERATURE CONTROLLER
TI - TEMPERATURE INDICATOR
PI - PRESSURE GAGE
BPR - BACK PRESSURE REGULATOR

Figure 24. Boiler test-loop boiler feedwater section

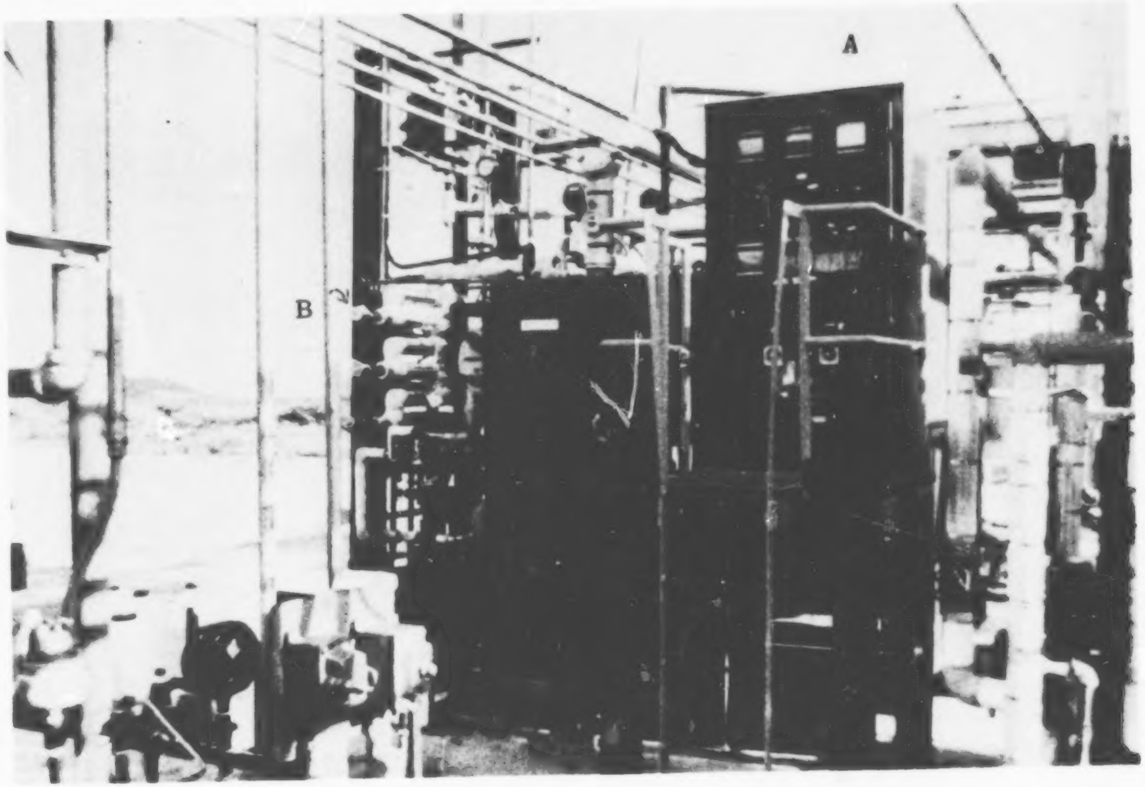


Figure 25. Pilot boiler control panel (A). Superheaters can be seen on the left (B).

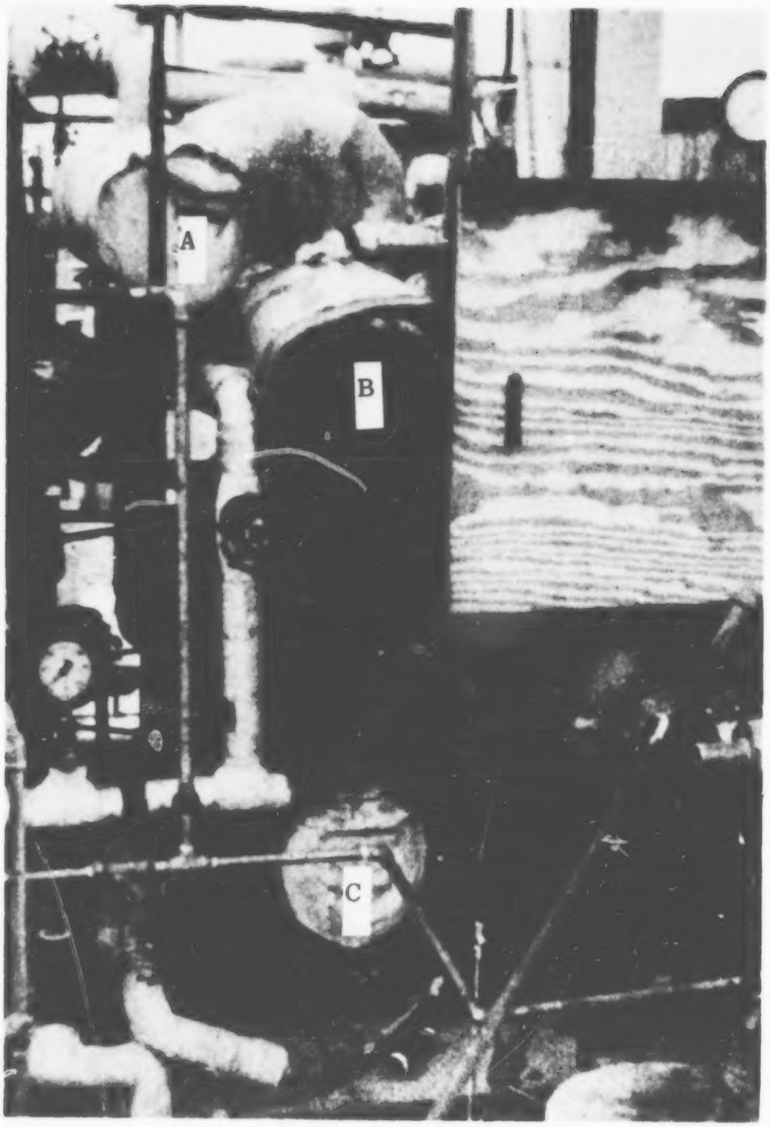


Figure 26. Backside of pilot boiler showing configuration: A) steam drum, B) boiler drum and C) mud drum.

All components of the boiler test loop except the pressure vessels and boil-off condenser were standard commercially available units.

At the conclusion of each boiler test run, the boiler was shutdown, and the heating element was removed, photographed, and sent to the laboratory for scale analysis.

INDIVIDUAL EQUIPMENT DESCRIPTION

Deaerator Feed Pumps

Small sliding vane rotary pumps delivered water from the feedwater storage tank to the deaerator. Each pump delivered 3.79 lpm (1 gpm) at 2.8 Kg/cm^2 (20 psig) recirculated excess flow back to the feedwater storage tank.

Chemical Feed Pump and Tank

A 5.68-l/hr (1.5-gph) adjustable rate diaphragm pump injected boiler water treatment chemicals into the boiler feed pump suction line. Chemicals were mixed in the chemical feed tank, and the pumping rate was adjusted to maintain proper chemical concentrations in the boiler. A back pressure regulator held constant pressure on the pump discharge to maintain accurate pumping rate control.

Hydrazine Feed Pump and Tank

A dilute solution of hydrazine was pumped by a diaphragm pump with a capacity of 5.68 l/hr (1.5 gph) into the feedwater as it left the deaerating heater. The pumping rate was adjusted to maintain the proper hydrazine residual in the boiler. A back pressure regulator held constant pressure on the pump discharge to maintain accurate pumping rate control.

Deaerating Heater

The deaerating heater was a 950-l (250-gal) atmospheric vessel designed to heat the incoming water to 100°C (212°F) to remove the majority of the dissolved oxygen and CO_2 from the boiler feedwater. Water level was maintained by a float operated level control valve. Outlet water temperature was maintained by the steam inlet control valve. Steam for the deaerator was supplied from the plant steam header.

Boiler Feed Pumps

The boiler feed pumps were positive displacement plunger pumps, each having a maximum capacity of 133 l/hr (35 gph). Pumping rate was adjustable to match the boiler demands. One boiler feed pump was designed to operate continuously while the other was turned on and off by the boiler level controller to maintain proper drum level. The feed pump, operating continuously, was set for slightly less than boiler requirements; the intermittent pump was set so that the combining pumping rate of both pumps was slightly greater than boiler requirements. Safety valves on each pump, set at 133.6 Kg/cm^2 (1,900 psig) protected pumps against overpressure in the event of discharge line blockage.

Boiler

The boiler and superheater were constructed of carbon steel and had a design pressure rating of 140.6 Kg/cm^2 (2000 psig) and a design superheater steam temperature of 399°C (750°F).

The steam generating section contained six electrical heating elements and the superheater section contained five heating elements. Steam output was determined by heating wattage. Characteristics of the different heating elements are shown in Table 18.

TABLE 18. CHARACTERISTICS OF HEATING ELEMENTS

	Wattage Watts	Heat Release BTU/hr/sq ft	Steam Output lbs/hr
Boiler High	9650	240,000	180
Boiler Medium	9600	180,000	180
Boiler Low	4915	100,000	90
Superheater	2200	22,000	-

Operating steam pressure was controlled by the steam back pressure control valve.

Superheated steam temperature was controlled by turning superheater heating elements on and off in response to the output signal from the temperature controller. Superheater heating elements were interlocked with the condensate flow signal to prevent operation unless steam flow past the heating elements exceeded a preset minimum.

Boiler drum level was maintained by the electrode type level controller which started and stopped the intermittent operating boiler feed pump, alarmed and shut off boiler heating elements on low level, and alarmed and shut off continuous operating feed pump on high level. A high pressure shutdown and alarm was activated if boiler pressure exceeded 126.6 Kg/cm^2 (1800 psig).

Continuous Blowdown System

Solids concentration in the boiler water was controlled by the blowdown timer which regulated the amount of time the blowdown valve was open.

Blowdown was cooled by a small water-cooled heat exchanger and collected in a graduated measuring pot.

Bottom Blowdown System

Sampling and blowdown of the boiler mud drum were accomplished by manually opening the blowdown valve. Blowdown was cooled by a small water cooled heat exchanger.

Saturated Steam Sampling System

Saturated steam samples were condensed by a small water-cooled heat exchanger and were collected manually.

Superheated Steam Condensing System

Superheated steam produced by the boiler was condensed in order to measure corrosivity of the condensate and to accurately measure boiler output. Where an adequate cooling water supply is available, this would normally be done with a water-cooled condenser. Since the boiler test loop was installed in a water-short area, the following equipment was used to minimize water usage.

Boil-off Condenser--

A stainless steel coil in an open vessel boiled off waste condensate from the boiler test loop at atmospheric pressure, thereby removing heat from the steam inside the coil.

Air Cooled Condenser--

Steam and condensate from the boil-off condenser were further condensed and cooled to approximately 71°C (160°F) by a fan-cooled air condenser.

Condensate Trim Cooler--

A small water cooled heat exchanger was used to cool the condensate to approximately 43°C (110°F).

Corrosion Test Loop

A series of pipe fittings was designed to hold four standard corrosion test coupons for evaluating corrosion characteristics of the steam condensate (Figure 27).

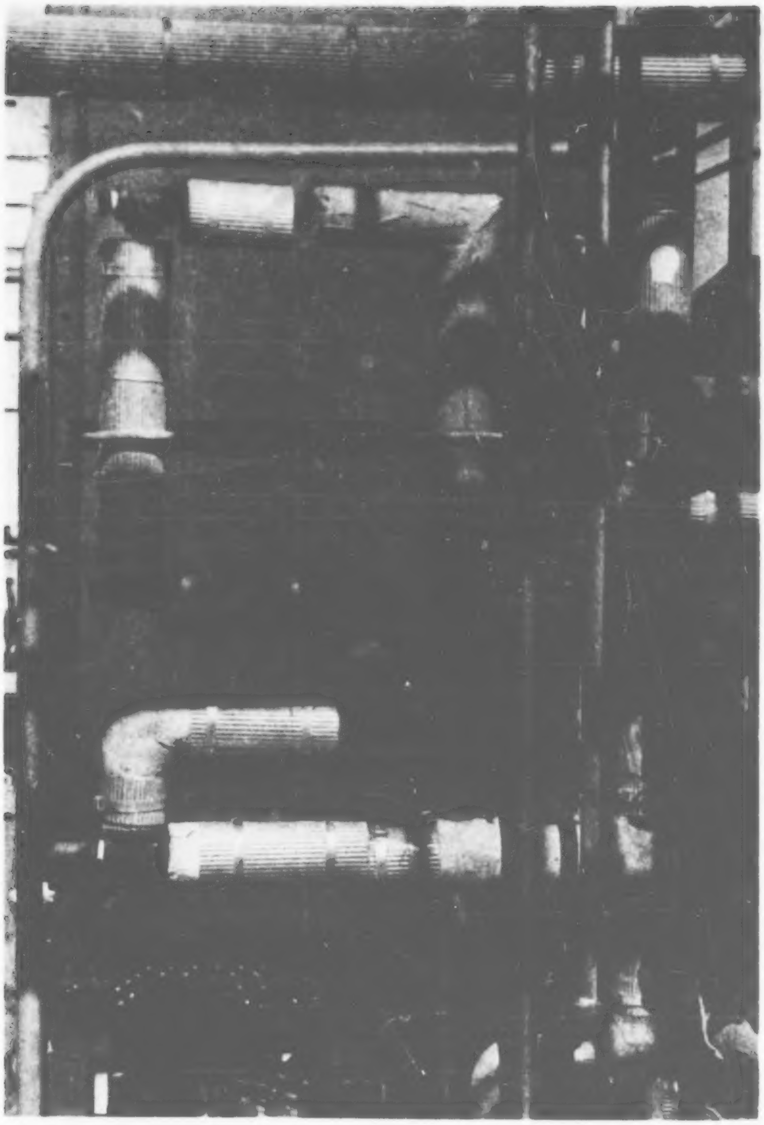


Figure 27. Boiler steam condensate corrosion coupon test loop.

TEST BOILER EXPERIMENTAL APPROACH

The primary objective of the test boiler studies was to determine whether the renovated wastewater would be suitable for use as boiler feedwater. Normally, the main concern about any feedwater impurity is its ultimate corrosivity and/or deposition potential within the primary steam generating area of a boiler. Acceptable practice conditions are based on the mineral consistency of the water (hardness, iron, copper) and the boiler design critiera. Because the water in question was derived from an organic-chemical plant wastewater that might still contain small quantities of organic chemicals, it was necessary to establish whether these chemicals would adversely affect not only the primary steam generating areas of boilers, but also the superheater section. It was also necessary to evaluate whether potentially volatile organic chemicals would carry into the steam supply and condensate systems and cause corrosion or deposition problems.

To this end, test boiler studies were completed that compared existing plant boiler feedwater (demineralized well-water) to renovated wastewater as boiler feedwater. The results of these experimental boiler studies were then compared to the actual and documented internal condition of the petrochemical plant boilers. The various full-scale plant boilers are typical 42.18 Kg/cm^2 (600 psig) wasteheat boilers, 77.84 Kg/cm^2 (1100 psig) CE tangentially fired power boilers, and 119.52 Kg/cm^2 (1700 psig) wasteheat boilers. These have been in service for six years using the same plant boiler feedwater (demineralized well-water) used to complete the experimental boiler studies. Although the test boiler was designed for 119.02 Kg/cm^2 (1700 psig) operation, it was necessary to limit actual operating pressure to 105.46 Kg/cm^2 (1500 psig) because of safety concerns with the drum level gage glass. It became apparent after repeated failures of the 240,000-BTU/hr/ft^2 heating elements during tests using demineralized well-water that the physical configuration of the test boiler would not allow evaluation of the renovated wastewater at these extremely high heat release rates.

Operating parameters chosen for primary investigation were 105.46 Kg/cm^2 (1500 psig) drum pressure, heat transfer rates of 180,000 BTU/ft^2·hr and 50 cycles of feedwater concentration within the boiler. The physical testing parameters were selected based on actual plant operation of the organic chemical manufacturing facility. Test boiler design controlled the steam flow to approximately 72 Kg (160 lb)/hr. Test duration was established at 2, 4, or 8 days, depending on individual test requirements. It was not a purpose of this study to evaluate treatment chemical performance. All tests were completed using accepted chemical treatment programs consisting of an oxygen scavenger (applied to the deaerator), a standard coordinated pH/phosphate internal boiler water treatment plus a proprietary blend of polymeric dispersants and antifoam agents for scale and foam control (applied to the boiler steam drum), and a proprietary blend of volatile amines for steam and condensate line corrosion protection(applied to the boiler steam drum).

SAMPLING AND ANALYSIS

Boiler feedwater, boiler blowdown water, steam, and steam condensate samples for each experiment were obtained every four hours during boiler operation. Boiler feedwater was monitored for hardness (calcium and magnesium ions), pH, conductivity and total organic carbon (TOC). The boiler blowdown was analyzed for conductivity, pH, alkalinity, phosphate, silica, iron and TOC. This was necessary to insure that pH and phosphate were maintained within the prescribed limits, and to accomplish this the chemical treatment was adjusted accordingly. Conductivity and silica analysis were completed for comparison to ABMA (American Boiler Manufacturers Association) prescribed standards. Steam and condensate samples were analyzed for conductivity, pH, silica and TOC to monitor general steam purity (sodium, silica, conductivity) and to determine the degree of organic carryover (TOC). While condensate analysis was another indication of steam purity, it was primarily used to monitor condensate corrosivity. Average values of the pertinent analyses for each boiler test are shown in Table 19. Analytical methods were conducted based upon Standard Methods (2), Methods of Chemical Analysis of Waster and Wastes (1) and Betz Handbook of Industrial Water Conditioning (4).

Scaling potential within the boiler was a major part of this study. The determination of deposition rate and volume consisted of quantitative analysis of the deposit formed on the high heat transfer area of the electric heat probes. The wet analytical methods employed for quantification of the deposit are described in Appendix D. The weight of boiler probe deposits were determined to enable comparison of deposit weights for the various experiments and the method is shown in Appendix E. The weights of probe deposits are listed in Table 20 for each successful boiler test run.

RESULTS AND DISCUSSION

To reiterate, the primary purpose of the investigation was to document corrosion and deposition potential of renovated wastewater when used as boiler feedwater, compared to demineralized well-water. Over twenty boiler tests were attempted. However, all but fourteen were aborted due to mechanical problems such as sight glass failures, safety valve failures, feed pump check valve problems and heating element failure. Eight additional experiments were considered invalid because of poor

TABLE 19. AVERAGE BOILER FEEDWATER AND BLOWDOWN ANALYSIS

	FEEDWATER					BOILER BLOWDOWN							
	pH	COND	TOC	MALK	TH	pH	COND	TOC	PALK	MALK	PO_4	SiO_2	Fe
Demineralized Well-Water													
Run 9	7.5	2	3	10	0	10.1	332	17	42	65	27	7	0.1
Run 17	7.7	1	-	0	0	8.3	127	3	11	37	16	5	0
Run 20	7.7	1	1	0	0	9.2	141	3	10	40	26	5	0.2
Renovated Wastewater													
Run 10	7.7	4	8	2	0	9.4	313	15	14	48	49	8	0.2
Run 12	7.6	3	14	0	0	9.5	146	5	23	55	36	11	0.1
Run 16	8.0	1	3	0	0	9.6	133	11	15	33	16	5	0.1

COND = Specific Conductance (µmho)
TOC = Total Organic Carbon (ppm)
PALK = P Alkalinity (ppm as $CaCO_3$)
MALK = M Alkalinity (ppm as $CaCO_3$)
TH = Total Hardness (ppm as $CaCO_3$)
PO_4 = Phosphate (ppm)
SiO_2 = Silica (ppm)
Fe = Iron (ppm)

TABLE 20. STEAM GENERATOR PROBE DEPOSIT ANALYSIS

Demineralized Well-Water	Test Duration (hours)	Probe A (g/m^2)	Probe B (g/m^2)
RUN NO.			
9	96	2.56	2.49
17	96	2.08	1.33
20	181	4.52	3.97
Renovated Wastewater			
RUN NO.			
10	62	0.78	1.00
12	96	0.65	1.18
16	192	0.45	0.47

chemical control. Chemical imbalances were believed to be due to residuals (magnesium oxide insulation) left after heating element failure and insufficient chemical cleaning between tests. Six valid experiments were completed; three in which plant boiler feedwater (demineralized well-water) was used, three in which renovated wastewater was used. All of the operational parameters (previously defined) were constant in these tests, except that of test duration. Test duration was varied so that deposition rate comparisons could be made between the feedwaters employed. The heat transfer rate of 180,000 BTU/ft^2·hr was selected as typical for an average radiant heat section of most industrial boilers constructed today. The operating pressure was set at 105.5 Kg/cm^2 (1500 psig). Tests were not run at lower heat flux or pressure levels because past practice has shown that as test severity is decreased, the potential for deposition within the boiler decreases.

Analyses listed in Table 19 indicate only subtle differences between the feedwater quality for each experiment. The differences listed may be in part "real" differences, or may reflect only analytical variability with the very high water quality. It must be emphasized that the analytical instrumentation and methods employed (pH, conductivity, TOC analyzer, alkalinity measurement) are significantly less sensitive when used for the analysis of very high purity water. These same variations may be to a large degree responsible for the differences seen in deposition weights listed in Table 20. However, all these differences fall within expected test deviations of boiler probe deposits.

A comparison of the feedwater analysis between the experiments using demineralized well-water shows little variation. A similar comparison of the feedwater analyses between the experiments using renovated wastewater also shows little variability but the levels of TOC are slightly higher. This does not preclude the use of renovated wastewater as boiler feedwater. A review of the analytical data for the boiler blowdown water shows no significant difference between any of the experiments reported (demineralized well-water or renovated wastewater). The differences recorded could easily be due to the subtle differences in the feedwater constituency or due to slight operational differences such as cycles of boiler water concentration or boiler steam flow.

The amount of deposit formed on the electric heater probes is shown in Table 20 and plotted in Figure 28. The total deposit listed is the sum of the individual components (calcium, magnesium, iron, phosphate and silica) that constitute boiler scale formed under the conditions employed in these experiments. The data obtained using demineralized well-water shows acceptable deviations between individual heater probe deposit weights within

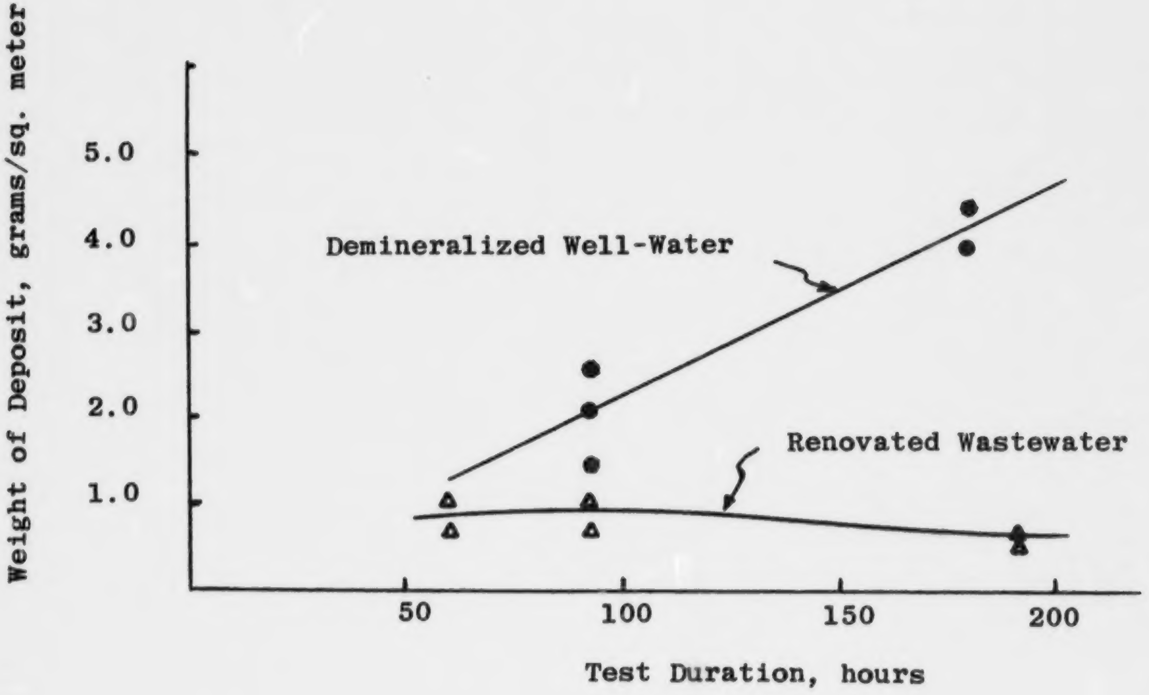


Figure 28. Test-boiler heater probe deposition.

single experiments, and between duplicate experiments under identical operating conditions (Table 20 - Tests 9 and 17). The differences seen are only subtle and likely to be caused by differences in feedwater constituency and/or operating parameters. The increase in deposit weight with time seen with the demineralized well-water is typical when tests are completed under severe operating conditions and/or when marginal chemical treatment is employed. The data obtained using renovated wastewater as feedwater exhibited similar scatter. However, when the renovated wastewater was used there was no significant change in deposit quantity with extended test duration (Figure 28). This is indicative of less severe operating conditions and optimum chemical treatment. The only difference between the two sets of data is that of feedwater employed; therefore, it can be concluded that the use of this renovated wastewater represents a lower scale potential than the demineralized well-water. Since the use of renovated wastewater as feedwater posed no greater deposition problem in the experimental boiler than the demineralized well-water, and because past experience has shown that the demineralized well-water presents no unusual scale problems in the full-scale plant boilers, it can be further concluded that the renovated wastewater should present no unusual deposition problems in the full-scale plant boilers.

In order to assess steam purity and potential superheater deposition, low heat flux (22,000 BTU/ft^2 hr) electric probes were installed into the boiler system to raise steam temperature from saturation 314°C (598°F) up to 390°C (750°F) superheat temperature. Steam samples were taken prior to the superheat section of the experimental boiler, and samples were taken of condensed superheated steam (return condensate). These data shown in Table 21 reveal some degree of contamination, but no significant difference between tests completed using either demineralized well-water or renovated wastewater. A review of the superheater probe deposits in Table 22 show no definitive differences in deposit quantity between experiments. It cannot be concluded absolutely from these experiments that either demineralized well-water or renovated wastewater will not impair boiler superheater operation. However, because the experiments completed using either feedwater gave similar results, it is expected that the renovated wastewater could be used in the full-scale plant boilers without problems any greater than those using existing plant boiler feedwater (demineralized well-water).

A corrosion test loop was installed in the return condensate line of the boiler system. Mild-steel and copper specimens were placed in the test loop for each boiler experiment conducted. Specimen weight loss was recorded and converted to average penetration rate. These data recorded in Table 23 using the calculation shown in Appendix F show a comparison between boiler tests using renovated wastewater and demineralized well-water. The data obtained from experiments when demineralized well-water was

TABLE 21. BOILER STEAM AND RETURN CONDENSATE ANALYSIS

	Boiler Steam				Return Condensate			
	pH	COND	TOC	SiO_2	pH	COND	TOC	SiO_2
Demineralized Well-Water								
Run 9	7.8	8	5	0.3	7.9	5	5	0
Run 17	7.7	2	-	0	7.9	2	-	0.1
Run 20	7.9	2	2	0	8.0	1	2	0
Renovated Wastewater								
Run 7	7.6	4	25	0.1	7.6	3	5	0.2
Run 8	7.6	8	8	0	7.8	8	6	0.1
Run 10	8.0	5	13	0	8.3	7	12	0.1
Run 12	7.9	3	1	0.1	8.0	5	1	0.1
Run 16	8.2	2	2	0	8.4	2	3	0

COND = Specific Conductance (umho)
TOC = Total Organic Carbon (ppm)
SiO_2 = Silica (ppm)

TABLE 22. STEAM SUPERHEATER PROBE DEPOSIT

Demineralized Well-Water	Test Duration (hrs)	Probe Deposit (g/m^2)
Run 9	96	.28
Run 17	96	.28
Run 20	181	.24
Renovated Wastewater		
Run 10	62	.34
Run 12	96	.36
Run 16	192	.21

TABLE 23. BOILER STEAM CONDENSATE CORROSION STUDIES

Demineralized Well-Water	Test Duration, hours	Corrosion Coupon Weight Loss, mils/year Mild-Steel	Copper
Run 17	96	6.3	4.2
		5.3	4.0
Run 20	181	1.2	0.6
		1.0	0.4
Renovated Wastewater			
Run 7	96	1.3	-
		1.1	
Run 8	96	3.4	-
		4.5	
Run 10	62	18.4	17.9
		16.3	17.1
Run 12	96	0.8	1.0
		0.6	1.2
Run 16	192	2.7	2.9
		1.9	3.5

evaluated revealed satisfactory corrosion control of mild steel and copper specimens (Tests 17 and 20). The data obtained from the experiments conducted using renovated wastewater show questionable corrosion control of both mild-steel and copper specimens in experiment 10 and good corrosion control in the other four experiments (7, 8, 12, and 16). A review of the condensate analysis does not show cause for the poor results in Test 10. While it cannot be concluded that condensate derived from renovated wastewater was more corrosive than condensate derived from demineralized well-water, it would be advisable to monitor corrosion rate when renovated wastewater is initially applied to the full-scale plant boilers.

From these pilot-scale boiler tests evaluating the feasibility of using renovated wastewater for boiler feedwater it is concluded that:

- Any impurities that passed through the wastewater treatment system did not noticeably affect boiler deposition; that is in comparison to impurities carried through standard plant demineralizer systems.
- The amount of waterside deposit when using renovated wastewater was less than that produced using plant boiler feedwater (demineralized well-water).
- The quality of steam produced from the renovated wastewater was equivalent to that generated from demineralized well-water.
- The amount of superheater deposition using renovated wastewater was equivalent to that produced using demineralized well-water.
- The condensate derived from using renovated wastewater as boiler feedwater appeared slightly more corrosive than did the condensate derived from demineralized well-water.

SECTION 6

CYCLE COOLING WATER TEST LOOP

A recycle cooling water pilot plant was operated in connection with the EPA test program to study the use of treated wastewater as makeup to an open, recirculated cooling water system.

Four treated wastewaters were studied:

1. Reverse Osmosis Permeate

2. Activated Carbon Effluent

3. Sedimentation/Filtration Unit Effluent

4. Clarified Activated Sludge Effluent

Both chromate and non-chromate corrosion inhibitors were studied to evaluate corrosion and/or fouling of carbon-steel (A-214), austenitic stainless steel (A-249) and Admiralty (B-111) heat exchanger tubes and test coupons.

An evaluation of any water for makeup to a cycle cooling water system requires an examination of several cooling system effects as well as their interactions, including biological fouling, corrosion and heat transfer characteristics. A particular water may, for example, produce good heat transfer but demonstrate excessive corrosivity, preventing its practical use as cooling tower makeup. Conversely, another water may produce low corrosion rates due to the formation of a protective type scale but have poor heat transfer characteristics. The cycle cooling water test program was designed to enable an evaluation of the major factors and effects controlling the use of a water as makeup as well as their relationships to each other. In this way an overall acceptability of a particular makeup water is determined.

GENERAL FACILITIES DESCRIPTION

The cooling water test-loop was designed to permit the evaluation of the scaling, fouling and corrosion effects of the renovated wastewater when used as makeup water. Standard, commercially available equipment was utilized in the assembly of the test facility. The primary components of the test-loop illustrated in Figure 29 are a cooling tower, heat exchangers with appropriate temperature measurement equipment, and steam condensate collection tanks.

Forced-Draft Cooling Tower

The cooling tower utilized in the test was a standard commercial, packaged, forced-draft cooling tower rates to cool 15 gallons per minute of water from 37.8°C to 29.4°C (100°F to 85°F) with an ambient wet-bulb temperature of 25.6°C (78°F). The cooling tower was rated for a maximum cooling capacity of 110,000 BTU/hr. The cooling tower, flow meters and acid/caustic storage tanks and feed pumps are shown in the photograph in Figure 30.

Acid/Caustic Feed Pumps

Positive displacement pumps rated to feed 1.9 liters (0.5 gallons) per hour fed acid or caustic as indicated by the pH meter/controller to maintain the desired pH of the circulating water.

Heat Exchangers

A 1.5 hp cooling-water circulating pump took suction from the cooling tower basin and pumped the cooling water through three double tube heat exchangers (Figure 31) operated in parallel and returned it to the cooling tower. Heat load was supplied on the shell side by reducing 200 psig steam to 8 psig. The three heat exchangers were approximately 76 cm (30 inches) long having a heat transfer area of 0.30 m^2 (0.323 ft^2) per tube. One heat exchanger was tubed with two carbon-steel tubes (A-214); one heat exchanger with two copper alloy tubes (B-111) and the third heat exchanger with two stainless steel tubes (A-249), thus permitting simultaneous evaluation of the effects of the water and inhibitors on different materials of construction. The heat-exchanger tubes were connected to the circulating water lines by a utility hose to prevent galvanic corrosion at the tube connection point, and to facilitate easy removal of the tubes for replacement, inspection, or cleaning.

Condensate Collection Tanks

Steam condensed on the shell side of each heat exchanger was collected in small condensate collection tanks. Each tank was equipped with level switches and timers to enable measurement of condensate flow for use in subsequent heat transfer coefficient calculations. Condensate collection tanks can be seen in the lower right corner of the photograph in Figure 32.

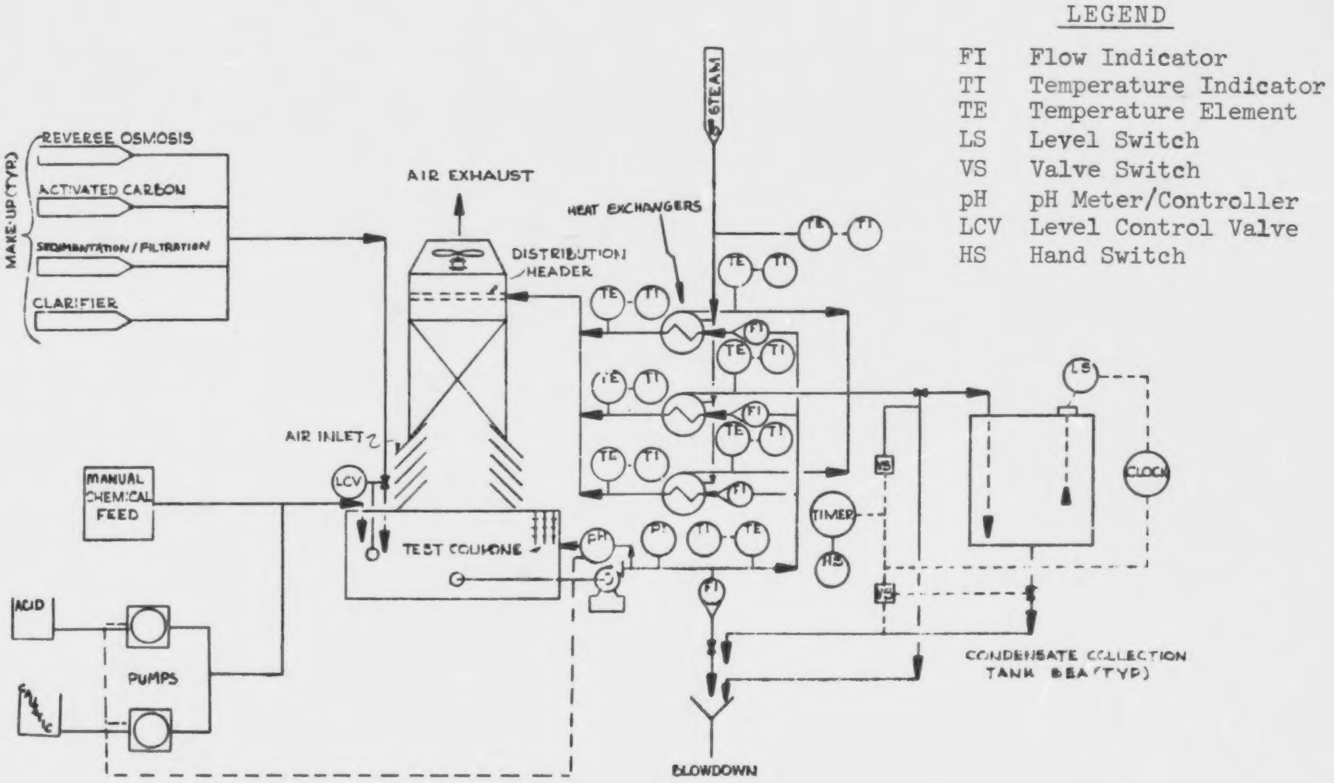

LEGEND
FI Flow Indicator
TI Temperature Indicator
TE Temperature Element
LS Level Switch
VS Valve Switch
pH pH Meter/Controller
LCV Level Control Valve
HS Hand Switch
MAKE-UP (TYP)
REVERSE OSMOSIS
ACTIVATED CARBON
SEDIMENTATION / FILTRATION
CLARIFIER
AIR EXHAUST
DISTRIBUTION HEADER
HEAT EXCHANGERS
STEAM
AIR INLET
LCV
MANUAL CHEMICAL FEED
TEST COUPONS
ACID
CAUSTIC
PUMPS
TE
TI
FI
PH
TIMER
HS
VS
LS
CLOCK
CONDENSATE COLLECTION TANK EA (TYP)
BLOWDOWN

Figure 29. Cycle cooling-water test loop facilities.

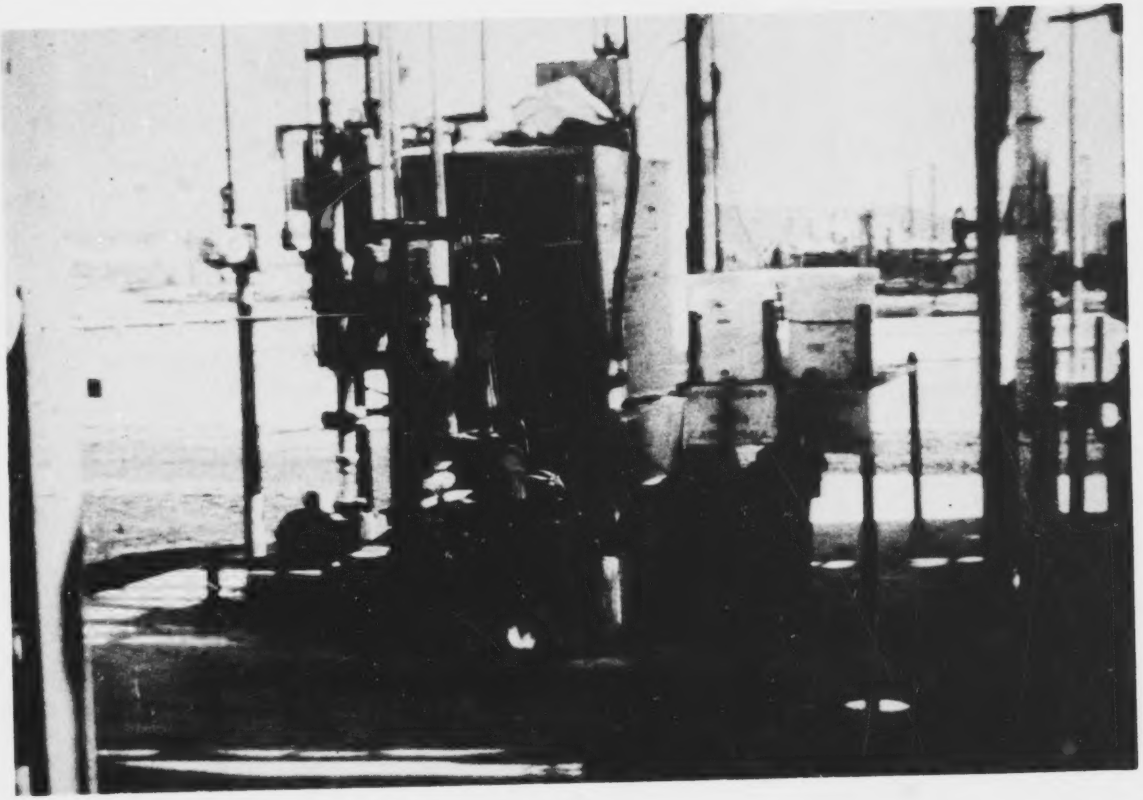


Figure 30. Forced-draft cooling tower and acid/caustic addition facilities

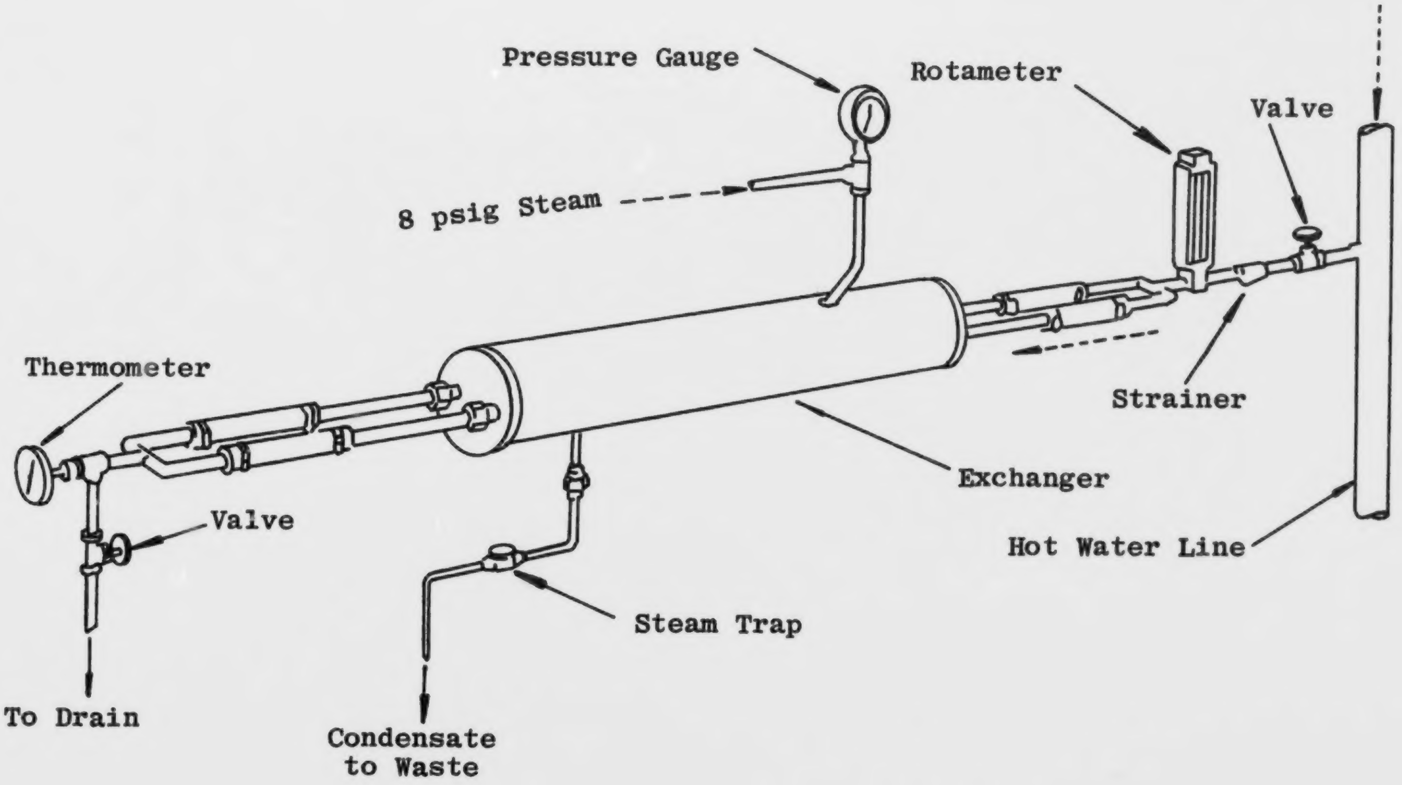

Pressure Gauge
Rotameter
Valve
8 psig Steam
Thermometer
Strainer
Exchanger
Valve
Hot Water Line
Steam Trap
To Drain
Condensate to Waste

Figure 31. Test heat exchanger.

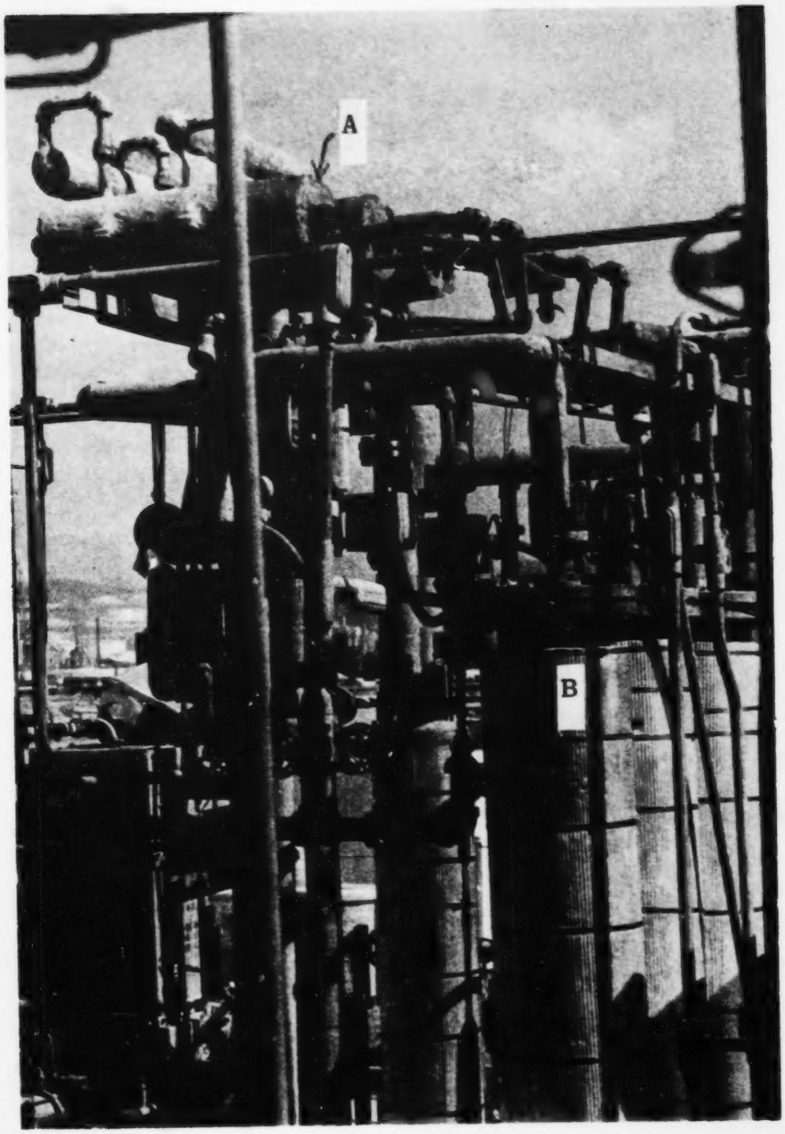


Figure 32. Cooling-water test loop heat exchangers (A) and condensate collection tanks (B).

SAMPLING AND ANALYSIS

Data were studied in the areas most important to evaluating the reuse feasibility of renovated wastewater in an open recirculating cooling water system. The cooling water test loop was monitored closely by a rigorous sampling and analysis program consisting of:

- Daily complete laboratory chemical analysis of makeup and cycle water.
- Field analysis of relevant factors several times per shift (e.g. chlorides, inhibitor, residual chlorine).
- Measurement of circulation rate and temperature differential several times per shift and calculation of evaporation rate, makeup and blowdown.

The recirculating cooling water system operated with a circulation rate of 95 lpm (25 gpm) and a temperature differential on the order of 8.3°C (15°F). Inlet water was about 29.5°C (85°F). The water velocity through the tubes was about 1.5 m/sec (5 ft/sec). At four cycles of concentration, the makeup was approximately 1.5 lpm (0.4 gpm), and the blowdown was about 0.4 lpm (0.10 gpm). Each test was preceded by an initial pretreatment of approximately 24-hour duration to effect cleaning and preparation of tubes for uniform inhibitor treatment.

COOLING WATER TEST EXPERIMENTAL APPROACH

Effluents from the reverse osmosis, carbon column, sedimentation/filtration unit, and secondary clarifier were used as makeup to the tower. The dissolved solids concentration in the circulating water was controlled at the desired level by blowing down a portion of the circulating water. The pH of the circulating water was controlled automatically by the injection of caustic or acid with a proportioning pump. Water-treating chemicals and biocides were added manually.

Each cooling water test was conducted over approximately 30 days. Both chromate (chrome/zinc) and non-chromate (zinc/phosphate) inhibitors were evaluated. Sodium hypochlorite was added to maintain 0.2 ppm free chlorine to control biological growth. The chemical treatments used for each test are summarized in Table 24.

TABLE 24. CHEMICAL TREATMENT FOR COOLING WATER PILOT TESTS

Test Run Number	Makeup Water	Dates	Chemical Treatment [(1)]	Chemical Control Level
#1	Reverse Osmosis Permeate	5/26 to 6/23 (28 days)	(A) Zinc/Phosphate Inhibitor (B) Phosphonate Dispersant (C) Phosphonate Inhibitor Sodium Hypochlorite Sulfuric Acid Sodium Hydroxide	3.0 ppm Zn 2 times (A) added G-10 ppm PO_4 pH 6.8-7.2 0.2 ppm Free Cl_2
#2	Activated Carbon Column Effluent	6/24 to 7/28 (34 days)	(D) Chrome/Zinc Inhibitor (B) Phosphonate Dispersant Sodium Hypochlorite Sulfuric Acid Sodium Hydroxide	25-30 ppm CrO, 2 times (D) added 0.2 ppm Free Cl_2 pH 6.2-6.8
#3	Activated Carbon Column Effluent	8/2 to 9/1 (30 days)	(A) Zinc/Phosphate Inhibitor (B) Phosphonate Dispersant (C) Phosphonate Inhibitor Sodium Hypochlorite Sulfuric Acid Sodium Hydroxide	Same as Test #1
#4	Sedimentation/ Filtration Unit Effluent	9/3 to 10/3 (30 days)	(A) Zinc/Phosphate Inhibitor (B) Phosphonate Dispersant (C) Phosphonate Inhibitor Sodium Hypochlorite Sulfuric Acid Sodium Hydroxide	Same as Test #1
#5	Sedimentation/ Filtration Unit Effluent	10/12 to 11/9 (28 days)	(D) Chrome/Zinc Inhibotor (B) Phosphonate Dispersant Sodium Hypochlorite Sodium Hydroxide Sulfuric Acid	Same as Test #2
#6	Clarified Activated-Sludge Effluent	11/11 to 12/8 (27 days)	Sodium Hydroxide Sulfuric Acid Sodium Hypochlorite	pH 6.8-7.2 0.5 ppm Free Cl_2

---

(1) All heat exchange equipment was pretreated with 600 ppm of a zinc/polyphosphate type inhibitor circulated for 4 hours at a pH range of 5 to 7. Following pretreatment, the system was blown down until the phosphate level was at 20 ppm.

- Measurement several times per shift of steam, condensate and cooling water parameters (pressure, temperature and flow, as appropriate).

The chemical analyses and the frequency collected on the inlet water and recycle water included:

Analysis	Frequency	Sample
Total Dissolved Solids	Daily	24-hr composite
Chlorides	Daily/Hourly	24-hr composite/grab
Hardness	Daily	24-hr composite
Alkalinity	Daily	24-hr composite
Sulfate	Daily	24-hr composite
Phosphate	Daily	24-hr composite
Iron	Daily	24-hr composite
Chromate	Daily	24-hr composite
Zinc	Daily	24-hr composite
Calcium	Daily	24-hr composite
Magnesium	Daily	24-hr composite
pH	Hourly	Grab
Residual Chlorine	1/Shift	Grab
Conductivity	Hourly	Grab

In addition to the chemical analyses, routine measurements were taken at various points in the process to enable sufficient data for mass balances and heat transfer calculations.

Corrosion Test Coupons

Test coupons constructed of A-214 carbon steel, A-249 stainless steel and B-111 admiralty brass were exposed to the recirculating cooling water in the cooling tower sump. Three racks with four coupons each of the three tested materials were initially exposed in each test. Coupons were removed in successive weekly intervals to observe and quantify the general corrosion rate as calculated by weight loss per unit time per unit area.

Heat Exchanger Tubes

Test heat exchanger tubes of A-214 carbon steel, A-249 stainless steel and B-111 admiralty brass were removed following each test run; the tubes were split, photographed before and after cleaning, pit depth and density measured, and scale thickness determined. The chemical composition of the scale was determined by analysis. A chemical mass balance was performed based on the average chemical analysis to quantify the chemical precipitation occurring within the system for correlation with other fouling test data. The heat exchangers were monitored routinely as follows:

Measurement	Frequency
Steam Flow, lbs/hour (calculated)	Every 2 hours
Steam Pressure, psig	Every 2 hours
Steam Inlet Temperature	Every 2 hours
Condensate Outlet Temperature	Every 2 hours
Water Flow	Every 2 hours
Water Inlet Temperature	Every 2 hours
Water Outlet Temperature	Every 2 hours

Heat Transfer Data

The coefficients of heat transfer were calculated from water and steam side data. Of the two values, the water side coefficient data was determined to be the most reliable. This value was plotted against time to delineate any loss of heat transfer during the test run. The fouling factor for deposition (R_s) was calculated as the difference of the reciprocals of the water side heat transfer coefficients between the termination and the beginning of the test run. In addition to the above steam and water measurements, the cooling tower was routinely monitored:

Measurement	Frequency
Recirculating Water Concentration	Every 2 hours
Circulation Rate	Every 2 hours
Inlet and Outlet Temperature	Hourly
Evaporation Rate (calculated)	Hourly
Blowdown Rate (calculated)	Hourly
Makeup Rate (calculated)	Hourly

Chemical Treatment and Controls

The levels of chemical inhibitor, dispersant and residual chlorine were measured and adjusted once per shift. The levels of these treatments maintained during each test are summarized in Table 24.

Biological Fouling

Biological factors were not investigated in depth; however, observations of the cooling tower fill and wood samples placed in the cooling tower sump were observed during each test run and the degree of biological fouling evaluated.

RESULTS AND DISCUSSION

Corrosion Data

Corrosion effects were determined by measuring the actual weight-loss of metal strips (coupons) of known initial weight removed from the cooling-tower sump each week, and by measuring the degree of pitting on the inside walls of the heat exchanger tubes. Individual general corrosion rates were calculated in mils/year and plotted vs. time of exposure in the tower sump (Figure 33) for A-214 carbon steel.

The effectiveness of the inhibitors tested was established in a test using activated sludge effluent with only pH adjustment and biological growth control (Test 6). The initial corrosion rate was high and increased during the first week with no added inhibitors. The decline in corrosion rate after the first week resulted from the formation of iron oxides which, after initial corrosion, redeposit to form a barrier-type corrosion protection. A 6.0 mil/year corrosion rate is probably the lowest that could be achieved with this wastewater without inhibitor addition.

Based upon the terminal general corrosion rate of each test, these cooling-waters, in a circulation system using 16-gage carbon-steel exchanger tubes and a corrosion allowance of one-half the wall thickness, would have a projected tube life as shown in Table 25. Only the activated sludge effluent without inhibitors showed unacceptable tube life, with RO permeate being marginal (assume 5 mils/yr as maximum acceptable corrosion rate). The RO test was not representative and, therefore, the results should not be concluded as unacceptable. It follows that RO as makeup would be acceptable with chrome/zinc treatment in that the activated carbon water which has a higher total dissolved solids content was acceptable.

In terms of corrosion and pitting of carbon-steel heat exchanger tubes, pitting was found to be the factor controlling exchanger tube life and the selection of chemical treatment. Pit depth and density in the exchanger tube measured mechanically following each test run are also shown in Table 25. Photographs of the split heat exchanger tubes, before and after cleaning are shown in Figures 34 through 45.

It appears that, from the standpoint of pitting, chrome/zinc was the only acceptable means of treatment for a carbon-steel system. Since A-249 stainless steel and B-111 admiralty brass showed negligible corrosion and pitting in all tests, the data are not presented. These materials would be suitable for all wastewaters and inhibitors tested from the standpoint of general corrosion.

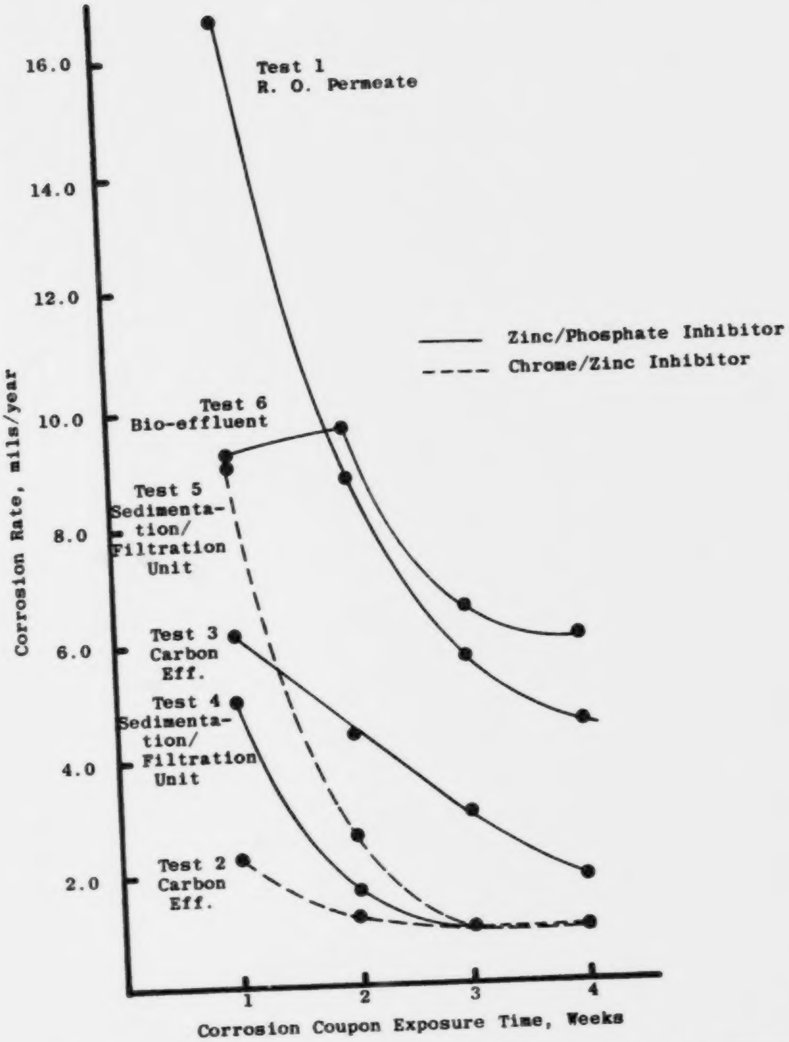


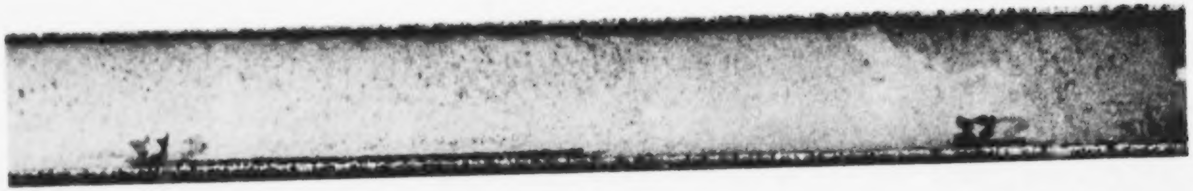
Figure 33. Corrosion rates for A-214 carbon-steel test coupons.

TABLE 25. CYCLE WATER TEST LOOP CORROSION DATA

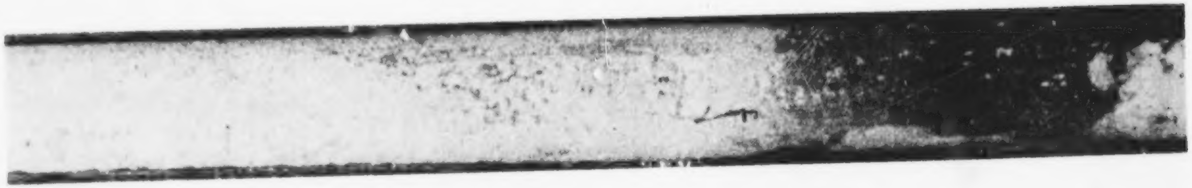
			Corrosion(1) A-214 Carbon Steel Coupons		Pitting(1) Heat Exchanger Tubes, A-214 Carbon Steel		
Test #	Cooling Water	Inhibitor	Terminal Corrosion Rate, Mils/Year	Tube Life, Yrs(2)	Maximum Pit Depth, Mils/Yr	Pitts Sq. In.	Tube Life, Yrs(2)
1	RO Permeate(3)	Zn/PO_4	4.5	7.1	144	15-20	.25
2	Activated Carbon Effluent	Cr/Zn	1.0	32	< 1.0	< 0.3	> 30
3	Activated Carbon Effluent	Zn/PO_4	1.8	17.1	60	4-5	.5
4	Sedimentation/ Filtration Unit Effluent	Zn/PO_4	1.0	32	60	2-3	.5
5	Sedimentation/ Filtration Unit Effluent	Cr/Zn	1.0	32	1.2	< 0.5	27
6	Clarified Activated Sludge Effluent	None	6.1	5.3	84	10-12	.3

(1) A-249 Stainless Steel and B-111 Admiralty brass showed negligible corrosion and pitting in all test runs.
(2) Based upon 16 gauge carbon steel heat exchangers tubes.
(3) Not representative of good RO treatment, membrane deterioration, chlorides in permeate 100-400 mg/1.

A-249 Stainless



B-111 Admiralty Brass



A-214 Carbon Steel

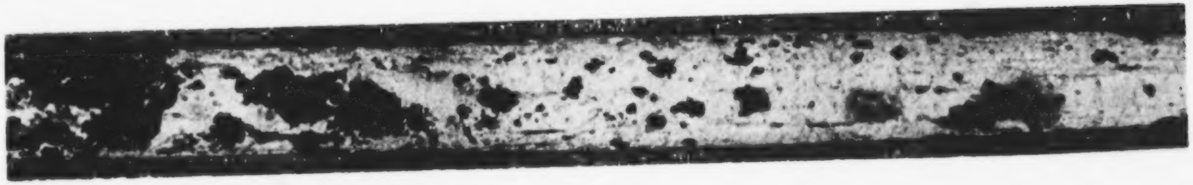
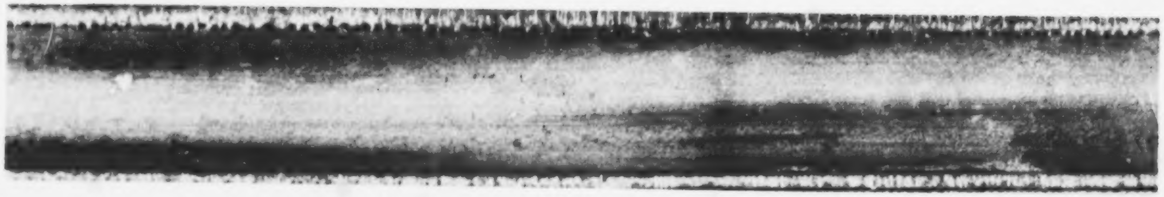


Figure 34. Run 1 Cooling-water test, R. O. permeate with Zn/PO_4 inhibitor. Heat exchanger tubes before cleaning.

A-249 Stainless



B-111 Admiralty Brass

A-214 Carbon Steel

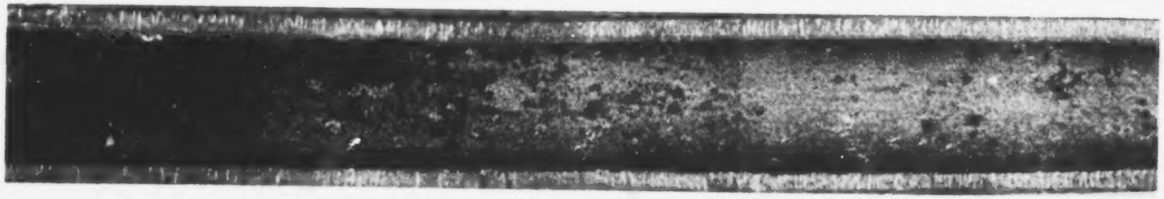
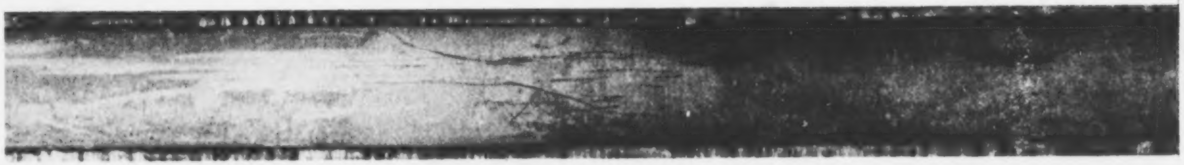
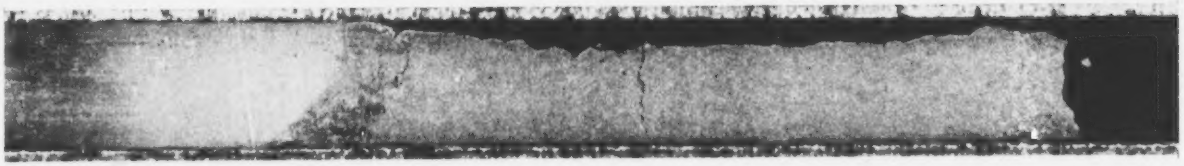


Figure 35. Run 1 Cooling-water test, R. O. permeate with Zn/PO_4 inhibitor. Heat exchanger tubes after scale removed.

A-249 Stainless



B-111 Admiralty Brass



A-214 Carbon Steel

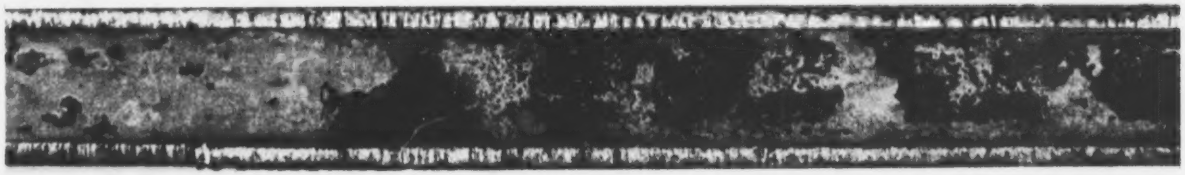


Figure 36. Run 2 cooling-water test, activated carbon effluent with Cr/Zn inhibitor. Heat exchanger tubes before cleaning.

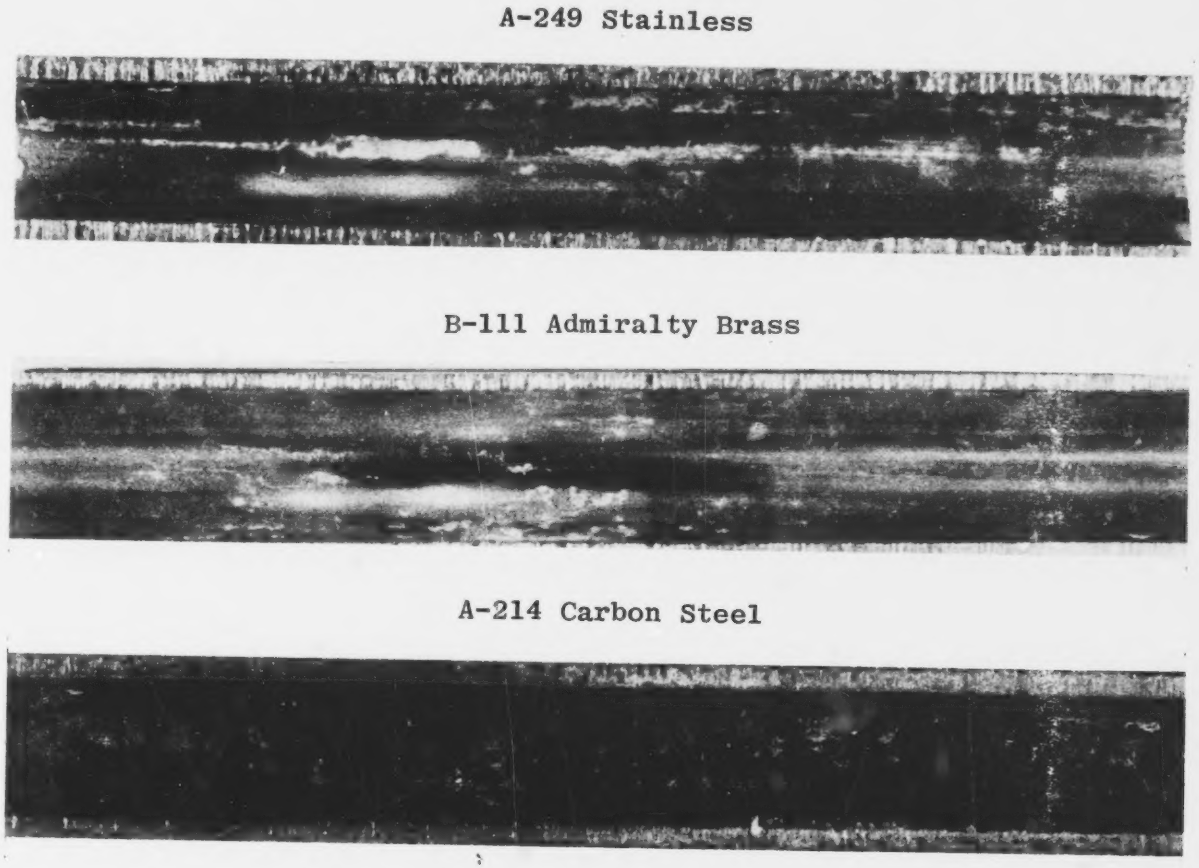
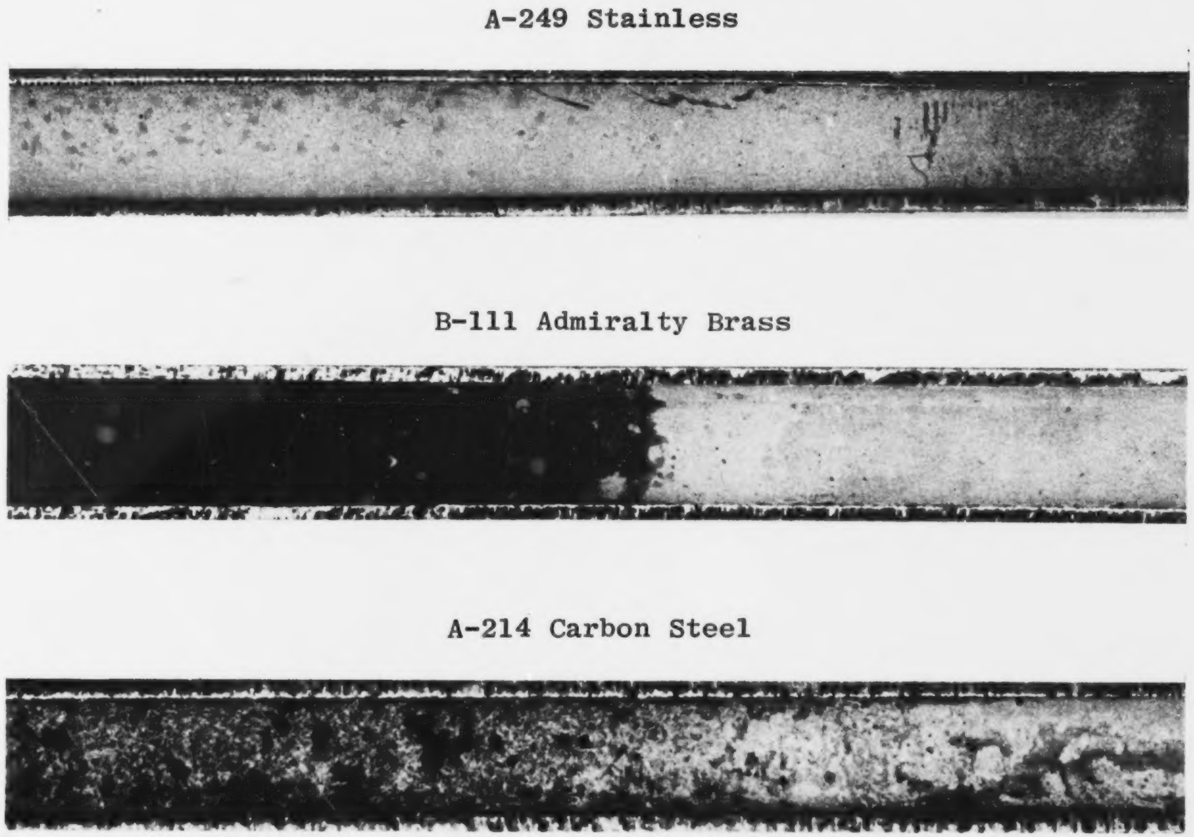

A-249 Stainless
B-111 Admiralty Brass
A-214 Carbon Steel

Figure 37. Run 2 Cooling-water test, activated carbon effluent with Cr/Zn inhibitor. Heat exchanger tubes after scale removed.



A-249 Stainless

B-111 Admiralty Brass

A-214 Carbon Steel

Figure 38. Run 3 Cooling-water test, activated carbon effluent with Zn/PO_4 inhibitor. Heat exchanger tubes before cleaning.

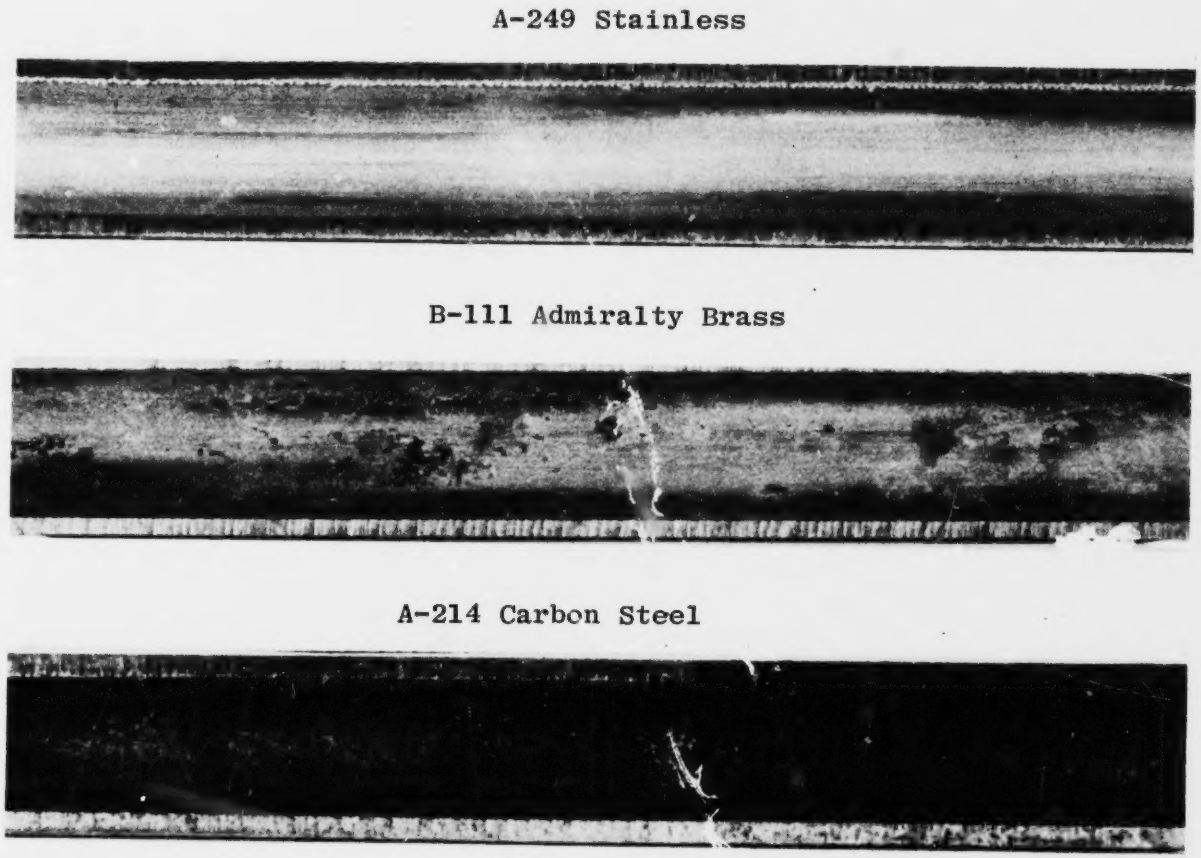
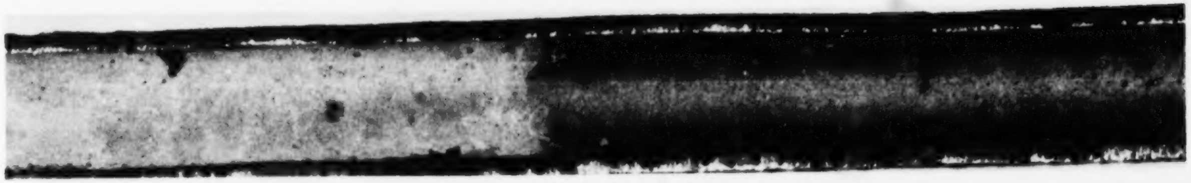
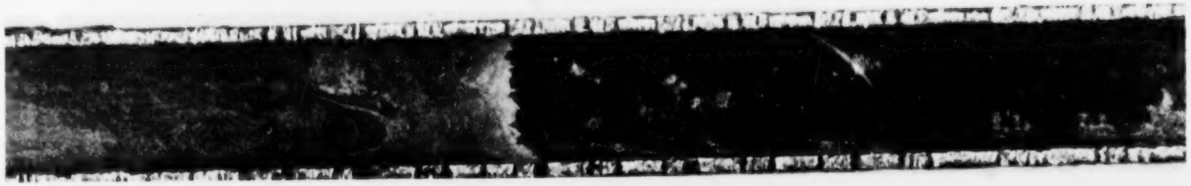

A-249 Stainless
B-111 Admiralty Brass
A-214 Carbon Steel

Figure 39. Run 3 Cooling-water test, activated carbon effluent with Zn/PO_4 inhibitor. Heat exchanger tubes after scale removed

A-249 Stainless



B-111 Admiralty Brass



A-214 Carbon Steel

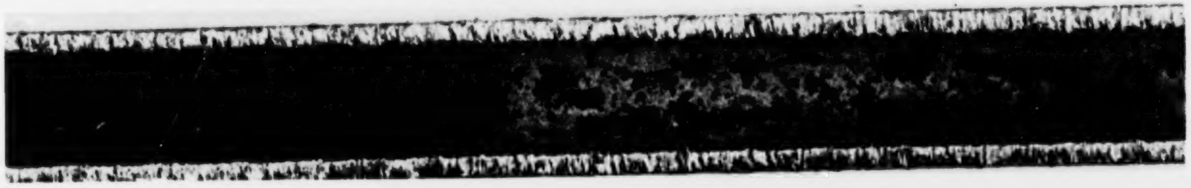
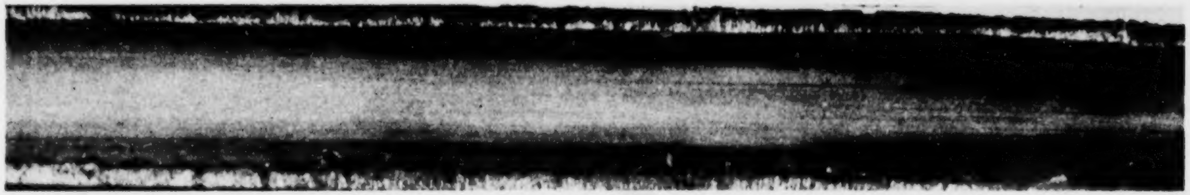


Figure 40. Run 4 Cooling-water test, sedimentation/filtration unit effluent with Zn/PO_4 inhibitor. Heat exchanger tubes before cleaning.

A-249 Stainless

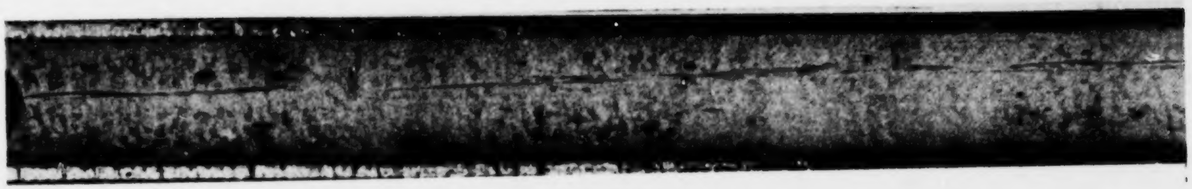


B-111 Admiralty Brass

A-214 Carbon Steel

Figure 41. Run 4 Cooling-water test, sedimentation/filtration unit effluent with Zn/PO_4 inhibitor. Heat exchanger tubes after scale removed.

A-249 Stainless



B-111 Admiralty Brass

A-214 Carbon Steel

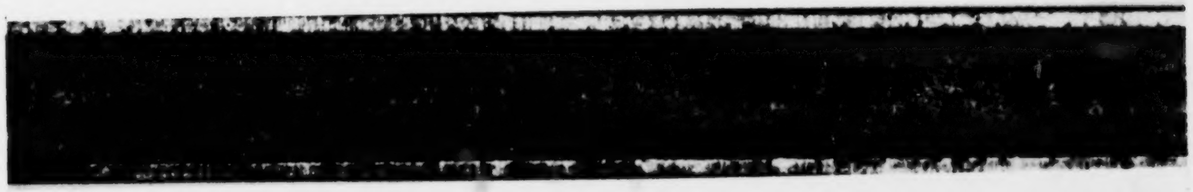


Figure 42. Run 5 Cooling-water test, sedimentation/filtration unit effluent with Cr/Zn inhibitor. Heat exchanger tubes before cleaning.

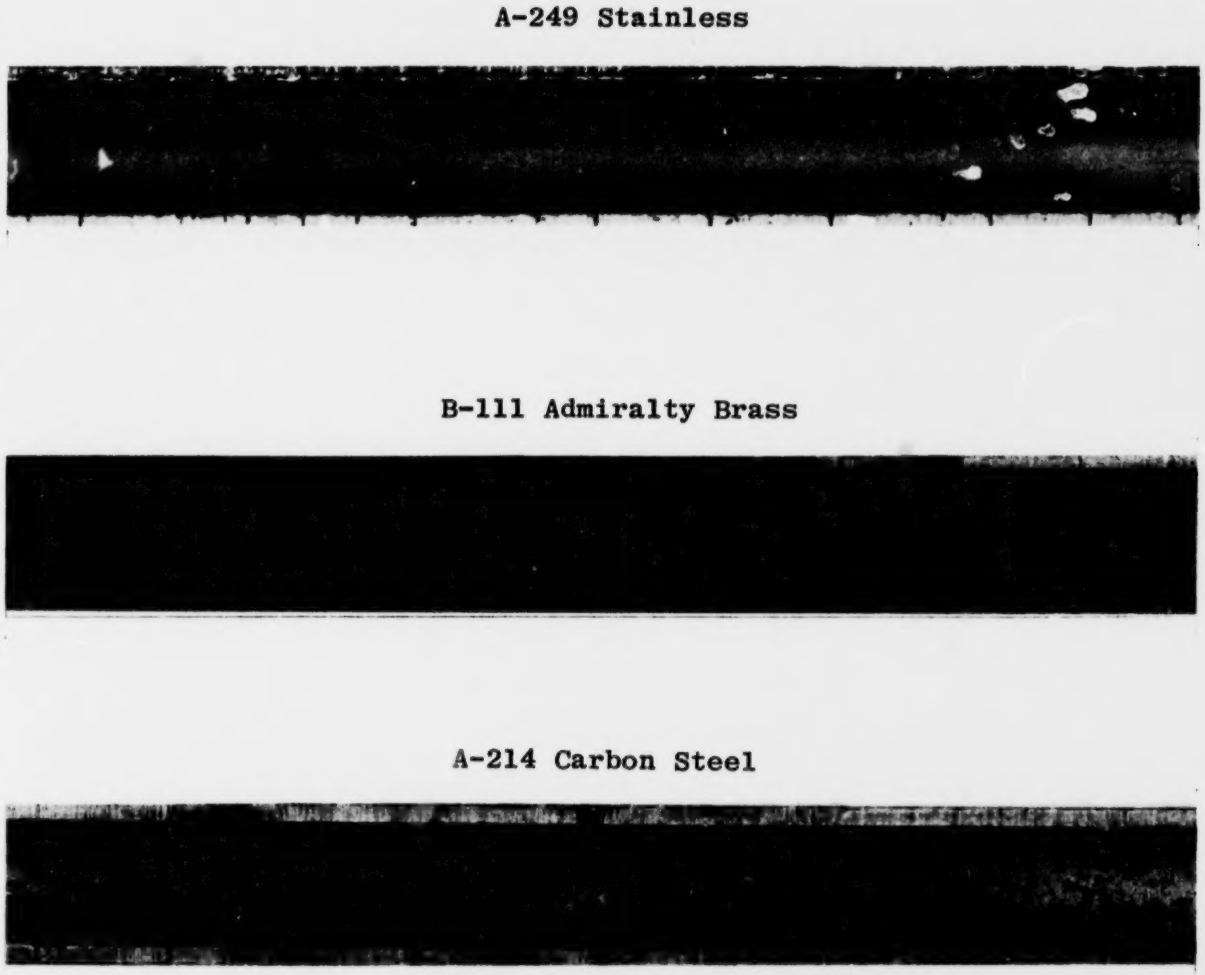

A-249 Stainless
B-111 Admiralty Brass
A-214 Carbon Steel

Figure 43. Run 5 Cooling-water test, sedimentation/filtration unit effluent with Cr/Zn inhibitor. Heat exchanger tubes after scale removed.

A-249 Stainless

B-111 Admiralty Brass

A-214 Carbon Steel

Figure 44. Run 6 Cooling-water test, biological effluent no inhibitors. Heat exchanger tubes before cleaning.

A-249 Stainless

B-111 Admiralty Brass

A-214 Carbon Steel

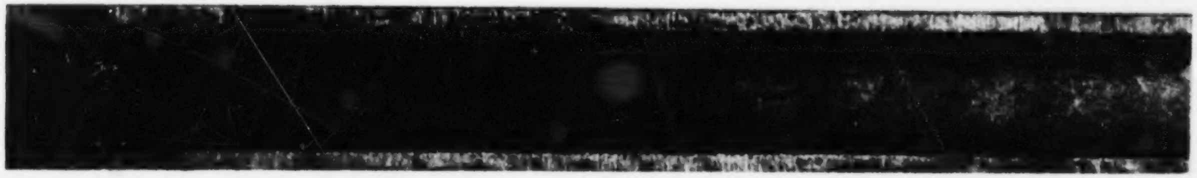


Figure 45. Cooling-water test, biological effluent no inhibitors. Heat exchanger tubes after scale removed.

Average Chemical Analyses and Mass Balance

The average chemical analyses for each run are listed in Table 26. These analyses represent the average of daily chemical tests during each test run. Using this data, the relative chemical precipitation of total hardness and phosphate was calculated based upon Run #4 which demonstrated the highest hardness/phosphate precipitation. For example, in Run #1 with 4 cycles of concentration (Cl) and a measured hardness in the feed of 45 mg/l the expected recycle concentration would be 4 x 45, or 180 mg/l. Only 145 mg/l was measured in the recycle, indicating 35 mg/l of hardness and precipitated. In Run #4, 103 mg/l of hardness precipitated, the highest degree of hardness precipitation for any of the test runs. Based upon a scale of 0 to 10 with 103 mg/l set at 10 the relative degree of hardness precipitation in Run #1 was $\frac{35}{103} \times 10$ or 3.4. This procedure was used to estimate hardness and phosphate precipitation for each test run (Table 27). These numbers indicate the relative degree of hardness precipitation, but do not necessarily mean that the higher numbers result in greater scale formation. They do mean that chemically, conditions were more ideal for scale formation. Other factors such as temperature, pH and velocity greatly affect the actual deposition of scale. Table 27 further indicates the relative degree of the formation of calcium sulfate scale as a function of the solubility product of calcium sulfate. In all test runs, except test #1 using RO permeate, the solubility product of calcium sulfate was exceeded indicating that a portion of the hardness was precipitated as calcium sulfate. The type of hardness precipitate will affect the heat transfer as well as corrosion rates, due to the physical characteristics of the scale formed.

Run #1, RO permeate with Zn/PO_4 inhibitor, indicated a somewhat lesser level of chemical precipitation than the other runs. The total dissolved solids were considerably lower in this test run than in other tests.

Comparison of test runs using activated carbon column effluent (Runs 2 and 3) indicated greater chemical precipitation in Run #2 using the Cr/Zn inhibitor. However, in Run #2 the total dissolved solids level in the recycle was nearly 85 percent higher than in Run #3. Had the total dissolved solids levels been equivalent, Run #3 using the Zn/PO_4 inhibitor would show a higher level of hardness precipitation.

The sedimentation/filtration unit effluent using Zn/PO_4 inhibitor (Run #4) showed the highest level of hardness/phosphate precipitation and exceeded the solubility product of calcium sulfate the least. Using the Cr/Zn inhibitor with this makeup water (Run #5) at comparable TDS levels, the

TABLE 26. AVERAGE CHEMICAL ANALYSIS

CYCLE COOLING WATER TESTS

Test Run Number	1		2		3		4		5		6	
Assay (ppm)	F(1)	R(2)	F	R	F	R	F	R	F	R	F	R
Total Dissolved Solids	1668	6685	3800	18,600	2733	10,100	3001	20920	3357	18,104	4348	19,872
Chlorides	320	1300	145	845	82	297	108	444	178	812	210	876
Cycles of Concentration based upon:												
Chlorides		4.0		5.8		3.6		4.1		4.5		4.2
TDS		4.0		4.9		3.7		7.0		5.4		4.5
Hardness as $CaCO_3$	45	145	48	207	77	241	60	143	50	264	91	352
Total Alkalinity as $CaCO_3$	170	60	530	160	1012	121	1030	296	1510	293	1337	670
Sulfate (SO_4)	120	2200	1288	9,612	387	5,251	585	7166	532	8,040	812	6336
Phosphate (PO_4)	8	12	17	22	24	54	43	81	14	45	13	23
Iron (Fe)	2	3.0	.18	.5	.12	.35	.17	.8	.2	1.1	.6	.9
Chromate (CrO_4)	-	-	-	36	-	-	-	-	-	28	-	-
Zinc (Zn)	-	12	-	5	-	5.5	-	4.2	-	4.4	-	-
Calcium (Ca)	12.6	40	13	60	22	67	17	40	14	73	25	98
Magnesium (Mg)	3.2	10	3	15	6	17	4	10	4	19	7	25
pH	7.9	7.2	8.3	7.3	8.3	6.8	8.4	7.5	8.6	7.2	8.5	7.4

(1) F - Feedwater

(2) R - Recycle

TABLE 27. CHEMICAL MASS BALANCE
CALCULATED RELATIVE CHEMICAL PRECIPITATION

CYCLE COOLING WATER TESTS

Test Run	Phosphate[(1)]	Hardness[(1)]	Excess of Calcium Sulfate Solubility Factor
#1. RO permeate Zn/PO_4 inhibitor	2.1	3.4	Not Exceeded
#2. Activated carbon effluent Cr/Zn inhibitor	8.1	6.9	4.9
#3. Activated carbon effluent Zn/PO_4 inhibitor	3.4	3.5	3.2
#4. Sedimentation/filtration unit effluent Zn/PO_4 inhibitor	10	10	2.6
#5. Sedimentation/filtration unit effluent Cr/Zn inhibitor	1.9	0	5.3
#6. Activated sludge effluent No inhibitor pH control only	3.4	2.9	5.6

---

(1) Based upon a scale of zero to 10 with Run #4 showing the highest hardness/phosphate precipitation.

hardness/phosphate precipitation was relatively low compared to Run #4; while the calcium sulfate solubility product was exceeded by more than twice that of Run #4. This data would indicate that the scale formed while using the Zn/PO_4 inhibitor would be primarily hardness/phosphate, while that formed using Cr/Zn inhibitor would be primarily calcium sulfate.

Using the clarified activated sludge effluent with no inhibitors added and only pH adjustment (Run #6) chemical analysis indicated hardness/phosphate precipitation as well as the greatest tendency of all runs to precipitate calcium sulfate.

Heat Transfer Coefficients

The effects of solids deposition on the heat transfer surfaces were evaluated by observing the decline in heat transfer during each test period. Data representing these observations is listed in Table 28. Heat transfer coefficients were calculated daily for both steam and water. Of the two values, the water-side coefficient was determined to be most reliable. The water-side coefficients were plotted with time to delineate the loss of heat transfer during each test run (Figures 46 through 51). The difference of the reciprocal of the terminal and initial heat transfer coefficients is the heat transfer resistance of the scale formed during the run, referred to as the fouling factor (R_S) and listed with the heat transfer coefficients in Table 28. The scale thicknesses measured and the appearance of the scale at the termination of each test run are also summarized in Table 28.

Based upon a maximum allowable fouling factor of .0010, both Runs #2 and #5 using Cr/Zn inhibitor demonstrated unsatisfactory to marginal heat transfer characteristics. Recall that Run #2 had a higher dissolved solids level in the recycle and would, therefore, be expected to deposit more scale. B-111 admiralty brass showed the greatest decline in heat transfer in all test runs except Run #1 using RO permeate and Run #4 using sedimentation/filtration unit effluent. A-249 stainless showed the lowest fouling factors and, therefore, the best heat transfer characteristics in nearly all test runs. Without the addition of any inhibitors or dispersants (Run #6, clarified activated sludge effluent) acceptable fouling factors were measured except with B-11 sdmiralty brass. Recall that corrosion and pitting was high in this test which would support the fact that without any protective scale formation heat transfer may be good but corrosion will be unsatisfactory.

One possible explanation for the lower corrosion and greater decline in heat transfer in the Cr/Zn test runs is that the formation of hardness/sulfate scale is more dense and stable than the phosphate/hardness scale formed when the Zn/PO_4 inhibitors are used. This is an important consideration in the selection of corrosion inhibitors.

TABLE 28. HEAT TRANSFER INFORMATION CYCLE COOLING WATER TESTS

Test #	Cooling Water	Inhibitor	Heat Transfer Coefficient (Water Side)						R_s (1)			Scale Thickness (mils) (2)			Scale Physical Characteristics
			Initial			Terminal									
			A-214	A-249	B-111	A-214	A-249	B-111	A-214	A-249	B-111	A-214	A-249	B-111	
#1	Reverse Osmosis Permeate	Zn/PO_4	440	400	385	335	340	375	.0007	.0004	.0001	9	5	6	Light Brown Rough Texture Soft
#2	Activated Carbon Effluent	Cr/Zn	460	440	360	240	225	180	.0019	.0022	.0027	7	4	18	Greenish White Uniform Scale Soft
#3	Activated Carbon Effluent	Zn/PO_4	420	430	410	310	385	210	.0008	.0003	.0023	4	9	14	Uniform Brown Deposit
#4	Sedimentation/ Filtration Unit Effluent	Zn/PO_4	525	505	570	495	450	470	.0001	.0002	.0004	3	< 1	4	Rough, Brown, Soft Deposit
#5	Sedimentation/ Filtration Unit Effluent	Cr/Zn	540	470	510	345	355	315	.0010	.0007	.0012	3	10	3	Grey White Scale with Rust Colored Spots
#6	Clarified Activated Sludge Effluent	pH Control Only	500	480	550	390	390	310	.0006	.0005	.0014	10	5	16	Thick Rust Colored Deposit

(1) The reciprocal of the difference in the terminal and the initial heat transfer coefficients representing the resistance of the scale formed to heat transfer (Fouling Factor).

(2) Measured average.

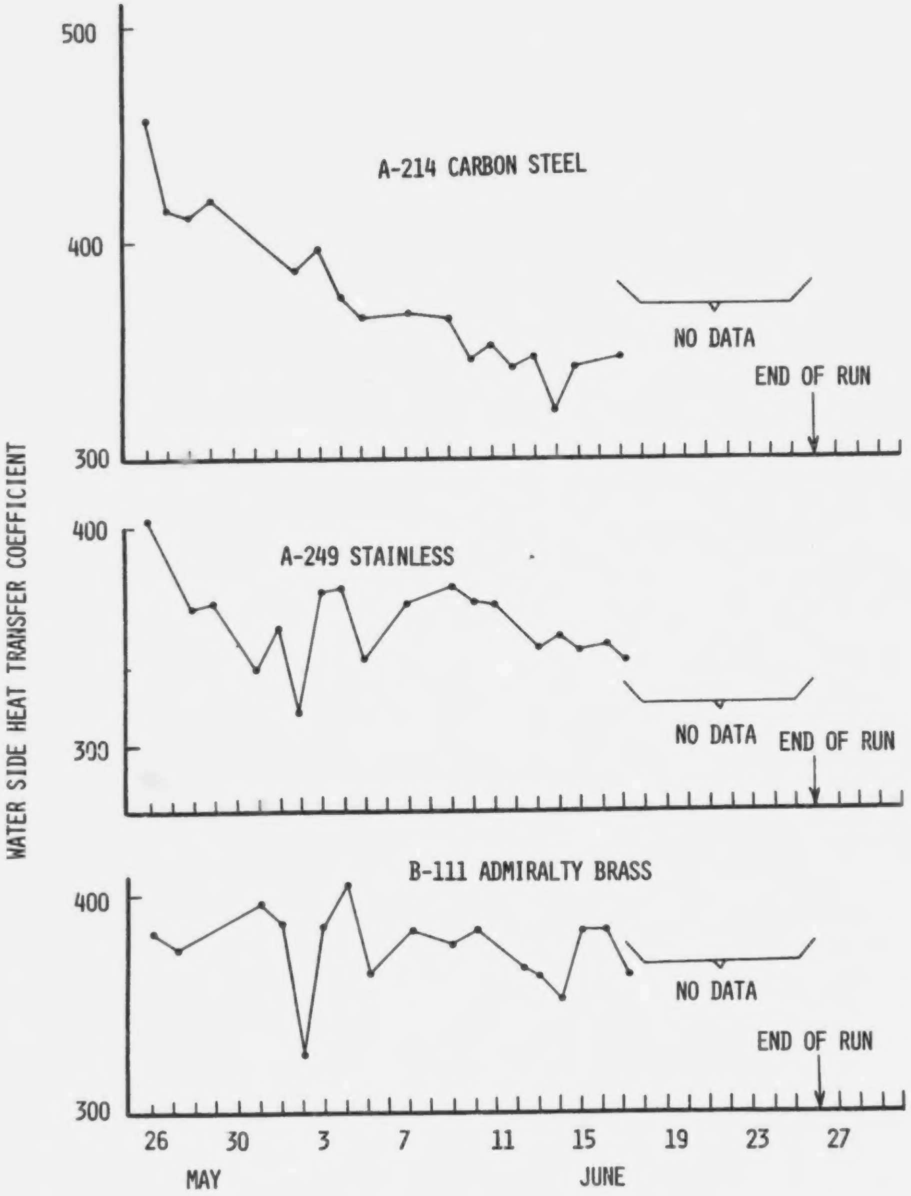


Figure 46. Water side heat transfer coefficients, Run 1, Zn/PO_4 inhibitor.

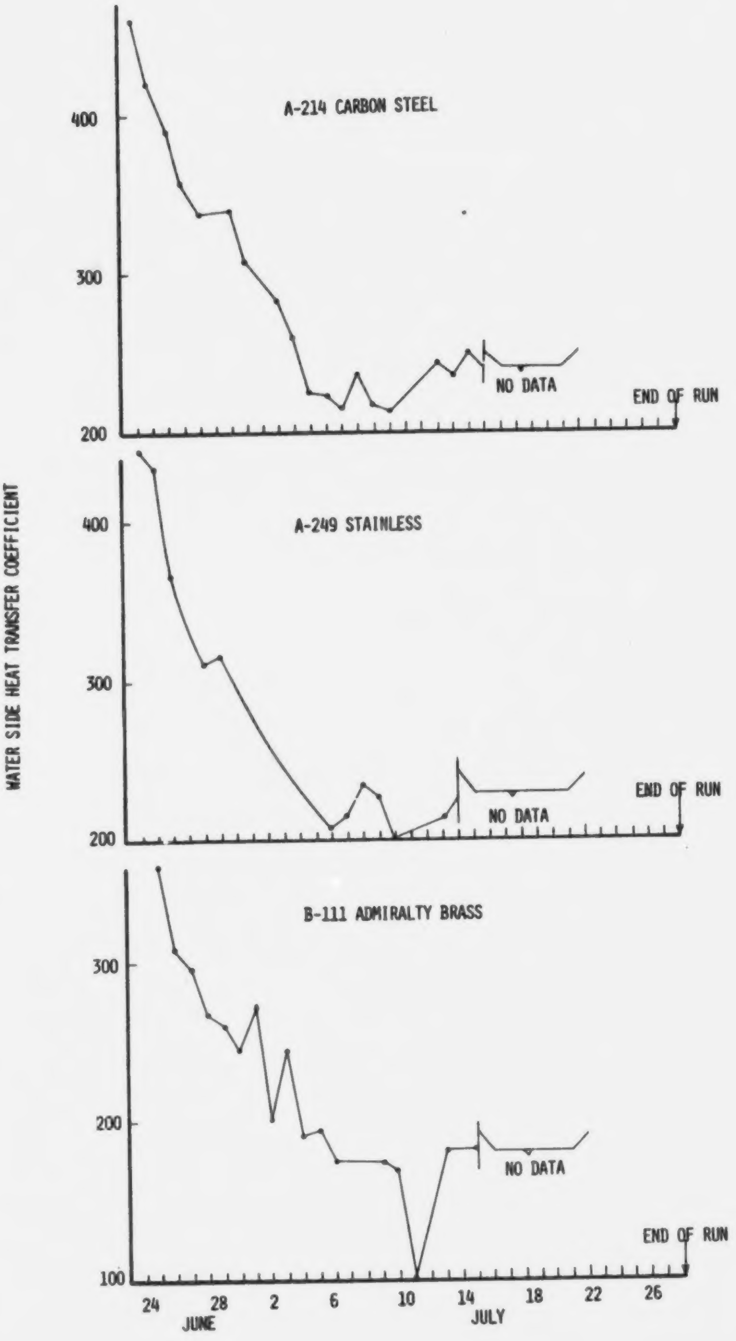


Figure 47. Water side heat transfer coefficients, Run 2, Cr/Zn inhibitor.

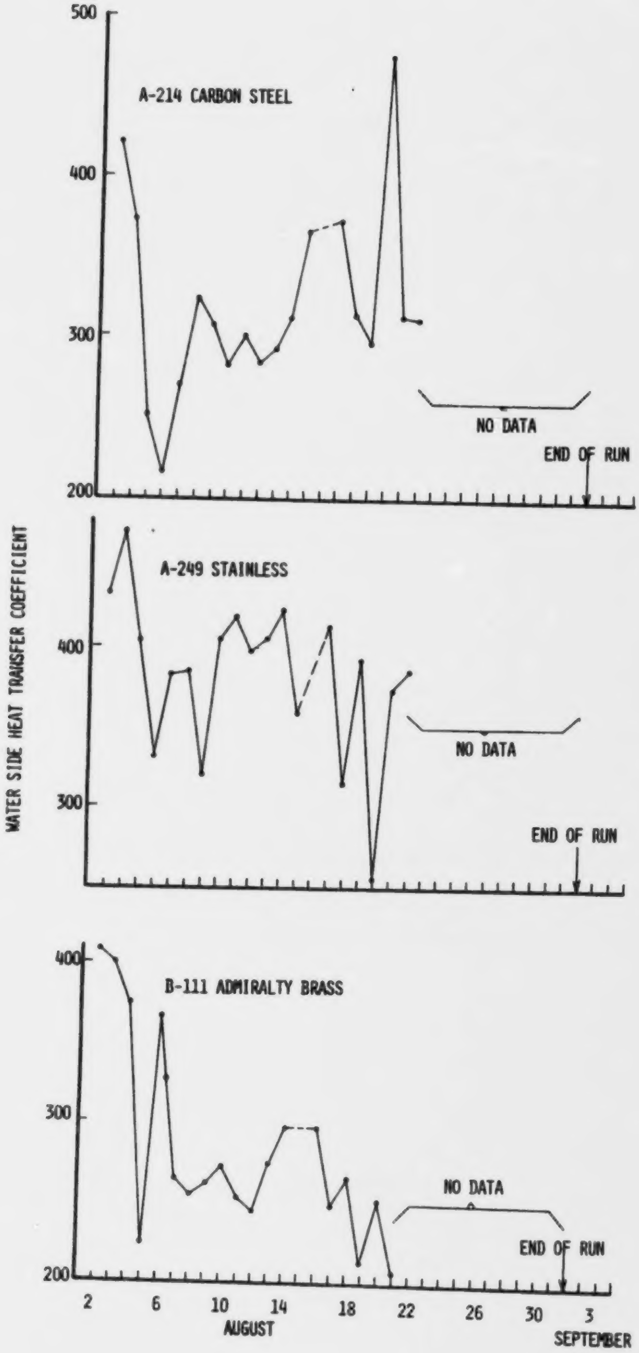


Figure 47. Water side heat transfer coefficients, Run 3, Zn/PO_4 inhibitor.

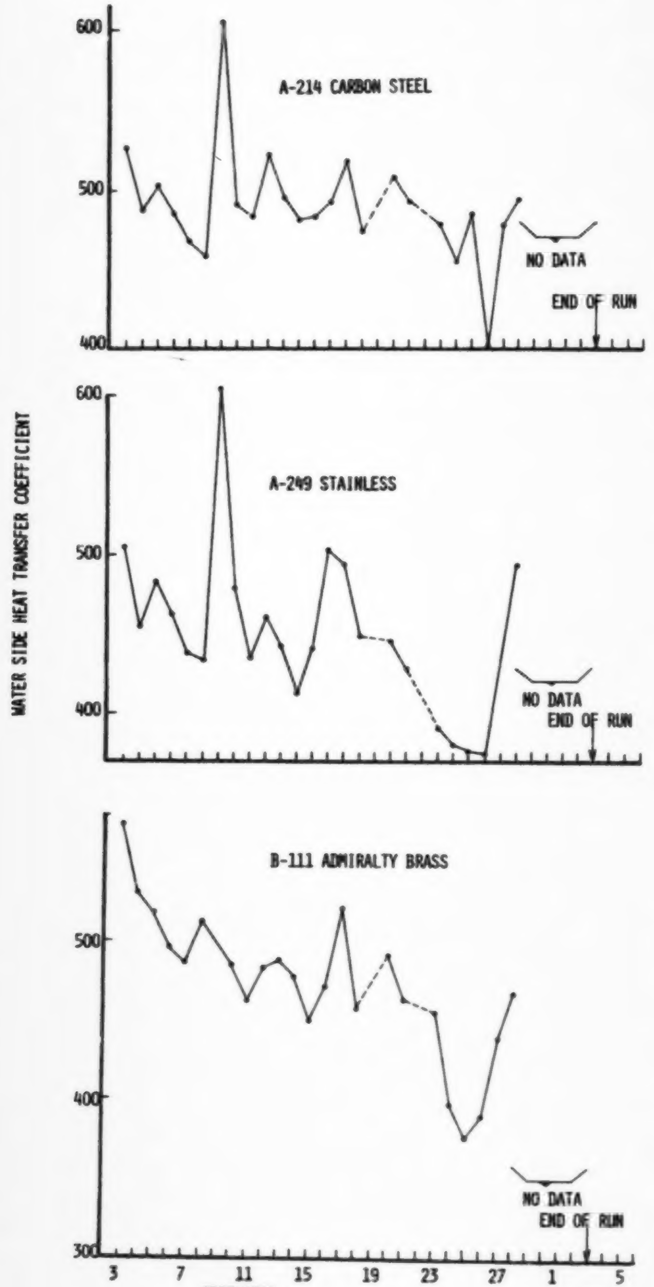


Figure 49. Water side heat transfer coefficients, Run 4, Zn/PO_4 inhibitor.

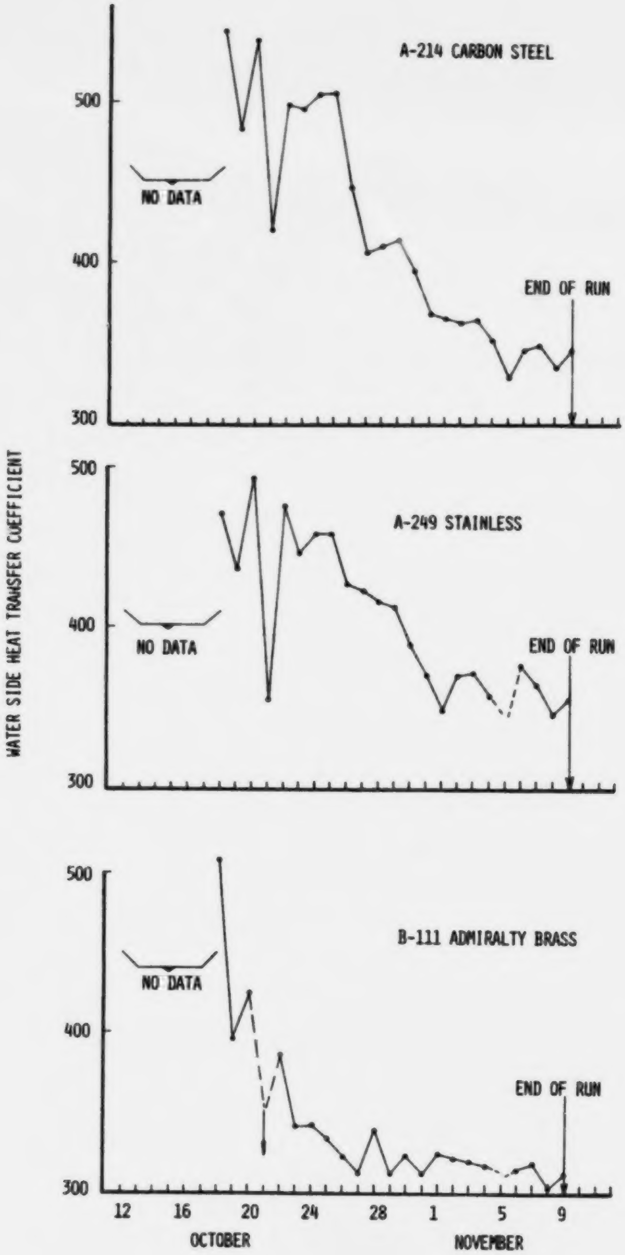


Figure 50. Water slide heat transfer coefficients, Run 5, Cr/Zn inhibitor.

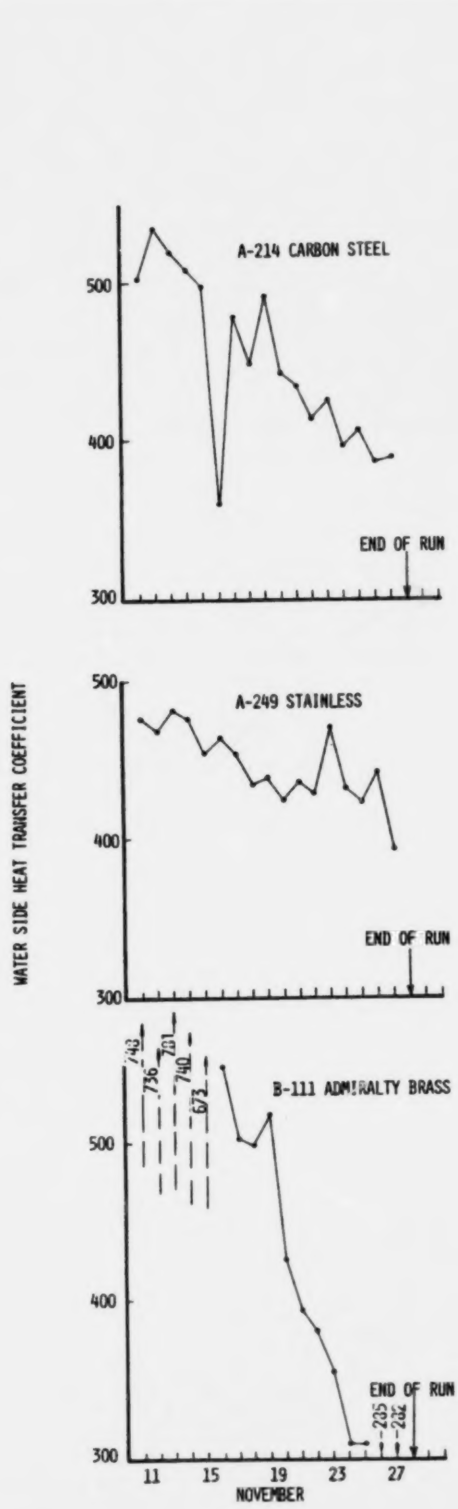


Figure 51. Water side heat transfer coefficients, Run 6, Zn/PO_4 inhibitor.

Biological Fouling

Wood samples placed in the cooling tower sump during each test run were examined for indications of severe biological fouling. No adverse biological effects were observed in any of the tests. Observations made of the cooling tower packing, wood samples and sump suggested normal biological growth. A detailed study of the biological growth was not undertaken in this program. However, biological growth was apparently effectively controlled with all makeup waters tested.

Summary of Cooling Water Test Conclusions

An examination of biological fouling, corrosion and heat transfer characteristics and their relations and interactions with each other is necessary for final evaluation of the use of a water for makeup to a cooling tower. Based upon the data collected and observations made in each of these areas, a summary of the acceptability of each of the various metals tested for each test run is summarized in Table 29. Conclusions based upon these findings should be limited to this specific study and do not necessarily reflect what would have been observed using other quality makeup waters, metallurgies, test conditions or chemical treatments.

1. Chromate treatment appeared to be effective in controlling the corrosion of A-214 carbon steel; however, the type of scale formed decreased the heat transfer characteristics to an unacceptable level, making this treatment unacceptable.

2. The use of Zn/PO_4 inhibitor resulted in satisfactory heat transfer on carbon steel but excessive corrosion resulted.

3. A-249 stainless steel and B-111 admiralty brass appeared to be acceptable in terms of corrosion, regardless of inhibitor treatment.

4. B-111 admiralty brass was unacceptable on heat transfer in all but two cases.

5. Biological fouling was effectively controlled in all test cases.

6. It appears from the data evaluated that only A-249 stainless steel was effective in maintaining satisfactory corrosion and heat transfer characteristics with the makeup waters and treatments tested and that special metallurgy would be required for the use of renovated wastewater as cooling water.

TABLE 29. SUMMARY OF ACCEPTABILITY OF MAKEUP WATERS TESTED WITH VARIOUS METALLURGIES

Makeup Water	Treatment	Metallurgies(1) Acceptable in Terms of			Overall Acceptable Metalurgy
		Heat Transfer	Corrosion	Biological Fouling	
RO Permeate	Zn/PO_4	A-214, A-249, B-111	A-249, B-111	A-214, A-249, B-111	A-249, B-111
Activated Carbon Effluent	Cr/Zn		A-214, A-249, B-111	A-214, A-249, B-111	
Activated Carbon Effluent	Zn/PO_4	A-214, A-249	A-249, B-111	A-214, A-249, B-111	A-249
Sedimentation/ Filtration Unit Effluent	Zn/PO_4	A-214, A-249, B-111	A-249, B-111	A-214, A-249, B-111	A-249, B-111
Sedimentation/ Filtration Unit Effluent	Cr/Zn	A-249	A-214, A-249, B-111	A-214, A-249, B-111	A-249
Clarified Activated Sludge Effluent	-	A-214, A-249	A-249, B-111	A-214, A-249, B-111	A-249

(1) A-214 Carbon Steel
A-249 Stainless Steel
B-111 Admiralty brass

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APPENDIX A: SPECIFIC ORGANIC ANALYSES - SAMPLE CONCENTRATION AND IDENTIFICATION PROCEDURES

Direct-Inject GC Analyses--An F and M, Model 810, chromatograph with a hydrogen flame ionization detector was used in all three GC analyses. These analyses included the use of: (a) a CARBOWAX 20M column for most volatile compounds, (b) a Porapak Q column for organic acids and (c) an OV-101 column for the glycol-trimethysilyl derivatives.

(a) Volatile Compounds:

The analysis for the volatile compounds was by direct-inject of the sample and employed the following conditions.

Column	CARBOWAX 20M (10%) on 80/100 AW Chromosorb W, 20 ft. by 1/8-inch O.D., stainless steel
Sample size	5 µl
Column Temperature	50 to 250°C
Program	at 10°C/min
Injection Port Temperature	220°C
Block Temperature	250°C
Helium flow	37 ml/min

Under these conditions, the components identified, eluted at the following times.

Compound	Elution Time, min.
Acetone	4.5
Methyl ethyl ketone	5.7
Toluene	10.2
Isobutanol	11.0
Ethyl benzene	11.5
n-Butanol	12.2
Cumene	12.5
Styrene	14.8
Acetophonone	23.1
Naphthalene	24.8
Phenol	34.1

These compounds were identified by a GC-mass spectrometric procedure after concentration using the method described. Quantification was established by use of external standards calibrated in the same range as specific compounds in the samples.

(b) Organic Acids:

In the organic acid analysis, the samples were pretreated prior to GC analysis to remove volatile compounds which could interfere in the determination. A 100-ml aliquot of the sample at ~pH 7-8 was evaporated to dryness using a Rotovac apparatus at 50°C and ~5 mm Hg absolute. Volatile organic compounds were removed from the residues in the Rotovac flask by this procedure. The residues in the flask were redissolved in 10 ml distilled water and adjusted to pH 2 with phosphoric acid. This solution of organic acids was used for GC analysis employing the following conditions.

Column	Porapak Q, 3 ft. by 1/8 in. O.D., H_3PO_4 treated, stainless steel
Sample size	5 µl
Column Temperature	175°C
Injection Port Temperature	240°C
Block Temperature	270°C
Helium Flow	37 ml/min

Under these conditions, the contained organic acids eluted at the following times.

Compound	Elution Time, min.
Acetic acid	1.8
Propionic acid	3.8
Isobutyric acid	7.4
Butyric acid	8.6

The acids were quantified using external standards in the same concentration range as in the samples.

(c) Glycols:

The samples for glycol determinations were concentrated and reacted with REGISIL to form trimethylsilyl derivatives. These glycol derivatives were analyzed by GC. This procedure for preparation of the derivatives (4) comprised charging a 50-ml aliquot of the sample to a distillation flask along with 150 ml pyridine containing 15 mg/l 1,4-butandiol. The 1,4-butandiol was used as an internal standard in the GC analysis. The flask was fitted to a distillation column and condenser, and 195 ml of distillate was removed at atmospheric pressure. The distillation flask containing 3 to 4 ml of residue was removed from the distillation column and cooled. REGISIL (1 ml) (Regis Chemical Company) was added to the residual pyridine. The flask was stoppered and allowed to stand for 15 minutes for reaction of the REGISIL and contained glycols. The pyridine solution of glycol REGISIL derivatives was employed in the GC analysis at the following conditions.

Column	OV-101 (3%) 12 ft. by 1/8-inch O.D., on 100-200 mesh Supelcoport
Column Temperature	50°C for 10 min.; 5°C/min. to 180°C
Sample size	5 µl
Injection Port Temperature	240°C
Block Temperature	260°C
Helium Flow	37 ml/min

Under these conditions, the glycols eluted at the following times.

Compound	Elution Time, min.
Ethylene glycol	12.1
Propylene glycol	13.6
1,4-Butandiol	19.9
Diethylene glycol	22.1
Ethoxytriglycol	26.2
Triethylene glycol	28.0

GC-Mass Spectrometer Analysis--The concentrating procedure for the GC-mass spectrometer analysis was that recommended by EPA (3). In the method, a 3-1 sample at ~pH 7 was transferred to a separatory funnel. Fifty milliliters of ethyl ether were added and the mixture was shaken for 1 minute. The sample then was extracted three times with 75-ml portions of methylene chloride, and the extracts were combined. The purpose of the ethyl ether was to improve the extraction efficiency of the more polar compounds like phenols and acids. The pH of the water layer then was adjusted to pH 2 using concentrated HCl and the methylene chloride extraction was repeated. Ethyl ether was not added a second time. When the second extraction was completed, the pH of the water layer was adjusted to pH 12 using saturated NaOH and was again extracted with methylene chloride. All extracts then were combined for drying and concentrating.

The ethylene chloride extracts were dried by pouring them through 2 inches of anhydrous sodium sulfate in a 19-mm ID glass column. The dried extracts were collected in a distillation flask and evaporated to ~5 ml using a Snyder column and steam bath. The concentrated extract then was transferred to an ampul and was further concentrated to ~0.5 ml in a warm water bath under a stream of clean, dry nitrogen. This concentrated extract was submitted for the GC-mass spectrometer analysis for identification of additional specific chemicals in the wastewater samples not detected by direct-inject GC.

APPENDIX B: WEEKLY AVERAGED DATA SUMMARIES

TABLE B-1 WASTE SLUDGE CHARACTERIZATION

Assay mg/1 (Detectable Limit)	Waste Secondary Sludge Dates 9/16	9/22	10/1	10/9	Avg	Sedimentation/Filtration Unit - Backwash Dates 9/16	9/23	10/1	10/9	Avg	Multi-Media Filter Backwash Dates 9/16	9/24	10/1	10/9	Avg	Carbon Column Backwash Dates 9/29	10/3	10/15	Avg
pH	7.5	-	7.9	8.2	7.9	-	-	8.4	8.5	8.4	8.6	-	8.4	8.5	8.5	8.5	8.4	8.6	8.5
COD	-	-	-	14241	14241	-	-	-	272	272	-	-	-	74	74	-	103	1000	550
TSS	13250	20710	11810	12100	14468	-	410	335	164	303	9	6	8	20	11	25	22	437	161
TDS	3178	3582	3620	3582	3491	-	3360	3658	3378	3465	2631	2732	3360	3230	2988	3542	3410	3504	3485
Ca	132	144	146	128	138	52	64	62	54	58	38	64	56	54	53	50	60	50	53
Li(1.0)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Mg	52	47	55	43	49	5.0	4.9	7.8	5.8	5.9	4.5	3.3	5.4	5.5	4.7	4.1	6.1	6.1	5.4
K(0.1)	74	86	104	70	83	14.0	2.0	2.1	2.1	5.0	5.0	0.5	0.9	1.5	0.9	0.7	1.8	0.2	0.9
Na	1220	1100	1330	-	1217	1010	1015	1202	1125	1088	965	785	1214	1260	1056	1240	1260	1138	1212
Cd (1.0)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
CrO_4	0.5	0.3	0.5	0.3	0.4	0.2	Nil	Nil	Nil	<0.1	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Cu (0.1)	0.9	0.9	1.0	Nil	0.7	0.1	0.1	0.4	Nil	0.1	Nil	Nil	0.3	Nil	<0.1	Nil	Nil	0.1	Nil
Fe	33	22	26	16.5	24	2.3	2.8	1.9	2.1	2.3	0.7	0.4	0.5	1.0	0.7	2.3	0.4	13.0	5.2
Mn (0.1)	0.8	0.7	0.9	0.0	0.6	0.1	0.1	0.1	Nil	<0.1	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Al	170	110	150	90	130	6.8	8.6	4.4	3.8	5.9	1.0	0.8	1.8	1.2	1.2	2.7	2.1	-	2.4
Ni (0.1)	0.5	0.5	0.5	Nil	0.4	0.1	Nil	0.1	Nil	<0.1	Nil	Nil	0.1	Nil	Nil	Nil	Nil	Nil	Nil
Zn (0.1)	2.4	1.7	3.6	3.1	2.7	0.1	0.2	0.2	0.1	0.15	0.2	0.1	Nil	0.2	0.1	0.1	0.2	0.1	0.1
Hg (0.05)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	-	Nil	Nil	Nil	Nil	-	Nil	Nil	Nil	Nil	Nil
As (0.1)	Nil	Nil	Nil	-	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	-	Nil	Nil	Nil	Nil	Nil
SiO_2 (Si)	(62)	(38)	(62)	(29)	(48)	2.0	2.0	1.6	3.0	2.2	1.0	1.5	1.0	-	1.2	1.3	1.0	5.5	2.6

TABLE 8-2 REVERSE OSMOSIS DATA SUMMARY, WEEKLY AVERAGES

		pH		Conductivity			Hardness		Fe			TSS
Date	Membrane	Feed	Perm	Feed	Perm	% REM	Feed	Perm	Feed	Perm	Feed	Perm
4/4-11	Tubular Cellulose Acetate	8.1	6.8	5703	1257	78.0	88	36.0	0.28	0.30	20.0	13.0
26-30		8.5	6.5	4377	809	81.5	100	5.0	-	-	6.0	2.0
5/1-7		8.5	6.9	5133	1167	77.3	40	4.0	-	0.13	7.0	18.8
8-14		8.4	7.0	4857	1192	75.5	44	8.0	0.00	0.10	29.0	40.3
15-21		8.4	6.8	4876	1121	77.0	44	3.0	0.08	0.02	3.3	0.7
22-28		8.4	7.3	5156	957	81.4	75	7.0	0.08	0.03	6.7	5.0
5/6/29-4		8.6	7.1	5444	1657	69.6	59	11.0	0.08	0.02	65.7	57.3
6/5-11		8.5	7.4	5289	1733	67.2	64	10.0	0.29	0.58	6.0	4.7
12-18		8.3	6.9	5223	1029	80.3	54	4.0	1.82	0.36	5.7	1.0
19-25		7.8	6.5	4956	553	88.8	69	5.0	1.22	1.49	4.7	0.0
6/7/26-2		8.1	6.3	5289	824	84.4	52	5.0	0.24	0.52	9.2	3.3
7/3-9		7.8	5.6	5477	731	86.7	41	6.0	0.23	0,29	13.5	0.3
AVG.		8.3	6.8	5148	1086	78.9	61	9	0.43	0.35	14.7	12.2
10-16	Spiral Cellulose Acetate	5.5	4.4	8273	324	96.1	63	0.0	1.56	0.34	15.0	0.0
17-23		8.0	5.6	5567	328	94.1	29	0.5	0.09	0.48	4.7	0.3
24-30		8.3	6.2	5200	607	88.3	17	3.0	0.26	0.38	5.7	0.0
7/8/31-4		7.8	5.9	4767	461	90.3	-	-	1.50	1.10	22.0	2.0
8/5-11		8.5	5.6	3627	297	91.8	68	2.0	0.30	0.45	10.0	1.0
12-18		8.3	5.4	3213	467	85.5	93	41.0	0.12	0.80	8.3	0.8
19-25		8.3	4.8	3656	431	88.2	75	1.2	0.14	0.05	6.0	0.0
8/9/26-1		8.5	6.1	3453	611	82.3	93	24.0	0.11	0.18	8.3	1.0
9/2-8		8.4	6.2	3133	535	82.9	92	12.0	0.51	0.61	5.5	1.0
9-15		8.3	6.5	3387	792	76.6	93	13.0	0.27	0.10	7.0	0.0
16-22		8.4	5.8	3133	515	83.6	74	2.0	0.90	0.59	7.0	0.0
23-29		8.3	6.2	3067	367	88.0	62	3.0	1.00	0.05	4.0	0.0
9/10/30-6		8.4	6.2	4867	733	84.9	33	0.5	0.29	0,15	6.0	1.4
AVG.		8.1	5.8	4257	498	86.3	66	8.5	0.54	0.41	8.4	0.58
10/7-13	Spiral Polyamide	8.3	7.1	9623	680	92.9	85	0.0	0.25	0.04	5.5	0.0
14-20		8.6	6.6	5144	480	90.7	32	0.0	0.51	0.20	8.0	0.0
21-27		8.7	7.6	4876	445	90.9	20	0.0	0.37	0.03	0.0	0.0
10/11/28-3		8.5	7.5	4133	367	91.1	33	0.0	0.25	0.25	17.5	4.0
11/4-10		8.6	7.7	5133	493	90.4	69	4.0	0.08	0.08	10.3	4.7
11-17		8.4	8.0	6300	462	92.7	75	1.0	-	-	20.0	-
18-27		5.5	5.1	5800	413	92.9	60	0.0	-	0.21	22.0	1.5
AVG.		8.1	7.1	5858	477	91.9	53	0.7	0.29	0.14	11.9	1.7

(Continued)

(TABLE 82 continued)

Date	Membrane	TDS			(TOC)COD			Silica		Chloride		
		Feed	Perm	% REM	Feed	Perm	% REM	Feed	Perm	Feed	Perm	% REM
4/4-11	Tubular Cellulose Acetate	4582	699	84.7	(109)	(23)	78.9	4.0	1.0	-	-	-
26-30		3212	459	85.7	(120)	(13)	89.2	-	-	-	-	-
5/1-7		3472	608	82.5	(39)	(5)	87.7	-	7.0	-	-	-
8-14		2986	673	77.5	(43)	(22)	49.5	5.0	3.8	-	-	-
15-21		3090	526	83.0	(11)	(7)	37.7	5.0	5.1	-	-	-
22-28		3719	721	80.6	(25)	(16)	36.0	7.2	4.6	-	-	-
5/6/29-4		3934	992	74.8	(28)	(11)	60.4	11.0	4.6	-	-	-
6/5-11		3717	997	73.2	(Nil)	(Nil)	-	11.1	5.7	-	-	-
12-18		4069	572	85.9	(28)	(25)	9.1	4.9	5.5	-	-	-
19-25		3660	111	97.0	(70)	(16)	77.9	15.9	6.8	-	-	-
6/7/26-2		3657	520	85.8	37	0	100.0	8.6	3.8	-	-	-
7/3-9		3881	431	88.9	59	6	89.2	9.8	4.1	-	-	-
AVG.		3665	609	83.3	(48)	(14)	70.4	8.3	4.7			
10-16	Spiral Cellulose Acetate	6846	156	97.7	34	12	64.7	17.0	1.0	229	38	83.4
17-23		3787	188	95.0	27	7	72.5	8.5	0.0	164	29	82.3
24-30		3690	382	89.6	68	8	88.2	9.0	4.7	147	57	61.2
7/8/31-4		3312	372	88.8	176	25	85.8	8.8	2.4	119	59	50.4
8/5-11		2468	249	89.9	39	0	100.0	12.1	4.2	72	27	62.5
12-18		2254	244	89.2	29	13	55.2	18.0	6.7	62	18	71.0
19-25		2040	254	87.5	32	11	65.6	13.3	8.0	92	23	75.0
8/9/26-1		2337	400	82.9	23	0	100.0	12.3	5.6	76	30	60.5
9/2-8		1933	317	83.6	34	0	100.0	10.8	5.6	56	20	64.3
9-15		1822	426	76.6	35	9	74.3	9.5	3.4	46	17	63.0
16-22		2038	330	83.8	17	27	-	10.4	2.5	49	14	71.4
23-29		2141	282	86.8	34	12	64.7	11.9	4.0	47	9	80.9
9/10/30-6		3350	469	86.0	30	5	83.3	7.0	3.2	111	43	61.3
AVG.		2924	313	89.3	44.5	10	77.5	11.4	3.9	97.7	29.5	
10/7-13	Spiral Polyamide	7929	485	93.8	134	14	89.6	9.4	1.5	264	43	83.7
14-20		3326	298	91.0	37	5	86.5	5.8	2.2	114	28	75.4
21-27		3509	310	91.2	51	5	90.2	5.2	1.3	106	28	73.6
10/11/28-3		3013	320	89.4	38	0	100.0	6.2	2.6	182	80	56.7
11/4-10		4127	311	92.5	27	5	81.5	4.8	1.0	467	86	81.6
11-17		4575	288	93.7	37	0	100.0	5.9	1.7	381	52	86.4
18-27		4950	329	93.4	8	2	75.0	8.7	2.7	171	41	76.0
AVG.		4490	334	92.6	47	4	91.5	6.6	1.9	241	51	78.8

TABLE B-3 ION-EXCHANGE DATA SUMMARY, WEEKLY AVERAGES

	4/26-30	5/1-7	5/8-11	7/22-28	8/9-17	8/22-31	9/1-6	9/14-27	10/1-18	10/23-29	11/1-9	11/14-20	AVG.
pH - RO Permeate	6.5	6.8	6.9	6.4	5.6	6.2	6.3	5.8	6.5	7.7	8.0	7.8	6.7
Primary Deionizer(1)	6.8	6.9	7.1	8.0	8.1	9.0	8.8	8.9	8.6	9.0	8.7	8.7	8.2
Secondary Deionizer(2)	4.3	-	-	6.6	6.9	7.6	8.9	8.0	7.1	8.9	8.0	7.7	7.4
Conductivity, umho - RO Permeate	607	897	950	411	467	360	285	445	402	387	425	560	516
Primary Deionizer(1)	738	752	1030	275	314	283	171	274	329	359	324	161	418
Secondary Deionizer(2)	-	-	-	5	9	4	9	-	3	-	2	4	5
Hardness - RO Permeate	4.7	22	12.2	3.0	41.0	3.0	12	2.4	0.3	0.0	3.2	4.0	9.6
Primary Deionizer(1)	7.0	3.4	8.0	5.5	28.0	17.0	28.0	7.0	0.5	0.0	2.5	7.5	9.4
Secondary Deionizer(2)	4.0	-	-	1.0	0.5	3.0	1.0	1.0	0.0	0.0	0.0	2.0	1.3
Iron - RO Permeate	-	0.13	-	0.33	0.8	0.05	0.41	0.50	0.20	0.04	0.08	0.00	0.25
Primary Deionizer(1)	-	-	-	0.10	0.07	0.13	0.12	0.50	0.21	0.00	0.00	0.00	0.13
Secondary Deionizer(2)	-	-	-	0.04	0.06	0.00	0.06	0.67	0.21	0.00	0.00	0.00	0.12
TSS - RO Permeate	1.6	3.2	2	0.0	0.8	0.0	0.0	0.0	0.0	0.0	4.5	0.00	1.0
Primary Deionizer(1)	0.0	2.6	4.7	0.0	0.7	1.0	0.0	0.0	0.3	0.0	3.6	0.0	1.0
Secondary Deionizer(2)	0.0	-	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.0	0.0
COD(TOC) - RO Permeate	(26)	(15)	(16)	24	13	12	26	26	12	10	4	0	14
Primary Deionizer(1)	(20)	(8)	(13)	15	18	21	8	28	-	7	3	11	13
Secondary Deionizer(2)	(10)	-	-	2	4	9	2	1	-	16	6	6	6
Silica - RO Permeate	-	7	4.5	3.0	6.7	4.0	5.4	3.6	2.8	2.0	1.0	2.1	3.8
Primary Deionizer(1)	-	-	3.5	2.8	5.4	8.0	2.5	3.2	1.9	5.3	0.6	0.4	3.4
Secondary Deionizer(2)	-	-	-	0.0	1.1	-	0.0	2.1	0.8	0.5	0.1	0.0	0.5
Chloride - RO Permeate	-	-	-	52	18	9	12	14	27	33	79	53	33
Primary Deionizer(1)	-	-	-	-	20	18	12	11	22	43	46	15	23
Secondary Deionizer(2)	-	-	-	-	2	1	1	0	< 1	3	6	2	1.8

(1) Weak Base Anion-Exchange

(2) Mixed Bed Ion-Exchange

APPENDIX C: SIZING OF FULL-SCALE FACILITIES FOR INVESTMENT COST AND OPERATING EXPENSE ESTIMATES

Suspended Solids Removal--

Suspended solids removal was accomplished in the pilot-plant using a package sedimentation/filtration unit that included flocculation, tube settlers and multi-media gravity filtration. Because of the low solids levels experienced and the ease with which they were removed in the pilot-plant these functions were estimated to be performed in the full-scale system by two solids contact clarifiers operated in parallel followed by three multi-media gravity filters operated in parallel.

Solids contact clarifier-- Each clarifier was sized for 75 percent of design flow. Diameter and depth are a vendor's recommendation based on flow rate and wastewater characteristics.

Equipment Data	Case A	Case B
Plant influent, m^3/min (gpm)	5.7 (1500)	11.4 (3000)
Design flow, m^3/min (gpm)	6.3 (1658)	12.6 (3315)
Diameter, m (ft)	13.7 (45)	19.8 (65)
Depth, m (ft)	4.7 (15.5)	4.7 (15.5)

Multi-media gravity filters--Three filters would be operated in parallel. Each filter was sized for 50 percent of design flow at a hydraulic loading of 0.16 $m^3/min \cdot m^2$ (4 gpm/ft^2). Filter dimensions were chosen to accommodate 4.1 m (13.5 ft) diameter rotary spray surface washes.

Equipment Data	Case A	Case B
Plant influent flow, m^3/min (gpm)	5.7 (1500)	11.4 (3000)
Design flow, m^3/min (gpm)	6.1 (1605)	12.2 (3210)
Filter area (each), m^2 (ft^2)	18.9 (203)	37.4 (403)
Filter width, m (ft)	4.7 (14)	4.7 (14)
Filter length, m (ft)	4.42 (14.5)	8.76 (28.7)
Polyelectrolyte @ 20 mg/l, Kg/yr (lbs/yr)	66,000 (145,500)	122,000 (270,000)
Polyelectrolyte cost, \$/Kg (\$/lb)	1.32 (0.60)	1.32 (0.60)

Activated Carbon Adsorption--

Effluent from the multi-media gravity filters would be pumped from the filter clear-well through a series of activated carbon columns. The columns would be arrayed in parallel trains of four columns in each. Within each train, three columns would be in service in series with the fourth on standby. When the lead column is exhausted, it would be taken out of service and the spare column placed in service as the final column. The carbon in the exhausted column would be regenerated on site. As in the pilot plant, the carbon bed depth in the full-scale columns was designed to be 4.88 m (16 ft) and the height of the cylindrical section of each column was 7.62 m (25 ft). A hydraulic loading of 0.163 $m^3/min-m^2$ (4 gpm/ft^2) is applied to the full-scale design.

Equipment Data	Case A	Case B
Plant influent flow, m^3/min (gpm)	5.7 (1500)	11.4 (3000)
Design flow, m^3/min (gpm)	5.8 (1526)	11.8 (3052)
Number of parallel trains	4	7
Column diameter, m (ft)	3.35 (11)	3.66 (12)
Bed area, m^2 (ft^2)	35.3 (280)	73.6 (793)

Activated Carbon Regeneration--

The spent carbon would be transferred from the columns to a dewatering and furnace feed tank. Regeneration would take place in a multiple-hearth furnace equipped with an afterburner and a wet scrubber. Regenerated carbon would be accumulated in a regenerated carbon storage tank. Virgin carbon makeup received in bulk would be inventoried with the reactivated carbon. The carbon would be transferred intra-unit by a water slurry. The furnace capacities were sized for a process stream COD removal of 93 mg/l, a carbon capacity of 0.334 Kg COD/Kg carbon and 60 percent on-line time.

Equipment Data	Case A	Case B
Plant influent flow, m^3/min (gpm)	5.7 (1500)	11.4 (3000)
Carbon exhaustion rate, Kg/day (lbs/day)	2300 (5070)	4600 (10,140)
Furnace capacity, Kg/day (lbs/day)	3800 (8377)	7600 (16,755)
Carbon attrition @ 7% loss per regeneration, Kg/day (lbs/day)	161 (354)	322 (708)
Carbon cost, \$/Kg (\$/lb)	1.32 (0.60)	1.32 (0.60)

Multi-media Pressure Filtration--

Effluent from the carbon columns would flow under pressure through two multi-media filters in parallel. The filtered water would flow into a surge tank with sufficient capacity to provide wash water for the carbon columns and pressure filters while maintaining a uniform flow into the reverse osmosis unit. Polyelectrolyte would be added just before the pressure filters via in-line static mixers. The pressure filters are sized for 50 percent of the plant influent flow and a hydraulic loading of 0.204 m^3/min-m^2 (5 gpm/ft^2).

Equipment Data	Case A	Case B
Plant influent flow, m^3/min (gpm)	5.7 (1500)	11.4 (3000)
Design flow, m^3/min (gpm)	5.7 (1500)	11.4 (3000)
Filter area, each, m^2 (ft^2)	14.8 (160)	29.7 (320)
Bed width, m (ft)	3.05 (10)	3.05 (10)
Bed length, m (ft)	4.85 (16)	9.76 (32)
Bed depth, m (ft)	1 (3.3)	1 (3.3)
Backwash storage tank, m^3 (gal)	490 (130,000)	590 (155,000)
Polyelectrolyte @ 20 mg/l, Kg/yr (lb/yr)	61,000 (134,000)	122,000 (269,000)
Polyelectrolyte cost, \$/Kg (\$/lb)	1.32 (0.60)	1.32 (0.60)

Reverse Osmosis--

Effluent from the pressure filters would be pumped from the pressure filter backwash tank to the reverse osmosis (RO) system. According to the manufacturer of the pilot-scale RO unit, the full-scale system would be arrayed in parallel trains each rated at 0.852 m^3/min (225 gpm). Unlike the batch-mode pilot operation, the full-scale reverse osmosis system would operate on a continuous flow, once-through basis using the spiral-wound polyamide membranes. The design salt rejection is 95 percent for 75 percent water recovery. Conservative design flow rates were used--6.4 m^3/min (1700 gpm) for the 5.7 m^3/min nominal flow case and 12.9 m^3/min (3400 gpm) for the 11.4 m^3/min nominal flow case. The entire system is located indoors.

Membrane replacement cost, included in the operating expenses, are based on a life expectancy of three years at an average cost of \$0.046/m^3 of product water (\$0.175/1000 gal).

Brine disposal facilities are not included in investment cost or operating expenses. However, viable solutions may be: ocean water disposal, solar evaporation, deep-well injection and mechanical crystallization and land fill. Likely, viable solutions for the Ponce, P. R. area are ocean (Caribbean Sea) disposal or solar evaporation.

Ion-Exchange--

Demineralization would be completed in an ion-exchange system. The reverse osmosis unit permeate would flow through cation exchange beds into the degasifier column and be collected in a clear well. The degasified water would then be pumped through weak base beds and strong base beds and into the demineralizer product storage tank.

The cation resins would be regenerated with sulfuric acid and rinsed with water from the clear well. The anion resins would be regenerated with sodium hydroxide and rinsed with demineralized water. The spent acid, and caustic would combine in a sump and be disposed of with the brine from the reverse osmosis unit. The final rinse waters would be comingled with the influent feed to the reverse osmosis unit. Storage facilities are provided at the site for 93 percent sulfuric acid and 50 percent caustic soda.

Equipment Data	Case A	Case B
Plant influent flow, m^3/min (gpm)	5.7 (1500)	11.4 (3000)
Design flow, m^3/min (gpm)	4.21 (1110)	8.42 (2220)
Resin beds:		
diameter, m (ft)	2.74 (9.0)	2.74 (9.0)
height, m (ft)	3.05 (10.0)	3.05 (10.0)
Number of beds: in-service (standby)		
cation	2 (1)	4 (1)
weak anion	2 (1)	4 (1)
strong anion	1 (1)	2 (1)
Regeneration frequency (beds/day)		
cation	2	4
weak anion	2	4
strong anion	1/7 days	2/7 days
Volume of beds:		
cation, m^3 (ft^3)	8.5 (300)	8.5 (300)
weak anion, m^3 (ft^3)	9.9 (350)	9.9 (350)
strong anion, m^3 (ft^3)	7.1 (250)	7.1 (250)

Equipment Data	Case A	Case B
Degasifier: number of columns	1	2
diameter, m (ft)	2.13 (7.0)	2.13 (7.0)
height, m (ft)	3.35 (11.0)	3.35 (11.0)
packing depth, m (ft)	2.13 (7.0)	2.13 (7.0)

Backwash Recovery--

Spent backwash from the gravity filters, pressure filters and carbon columns would be treated in a backwash recovery system prior to being recycled to the secondary treatment system. Spent backwash streams would be combined in a collection sump. Water would be pumped out of the sump to a two compartment, agitator tank, where a polymer flocculant would be added in the first compartment and with flocculation taking place in the second compartment. The flocculated stream would flow to a clarifier with the clarifier overflow recycled to the head of the secondary treatment system.

Equipment Data	Case A	Case B
Design (influent flow m^3/min (gpm)	5.7 (1500)	11.4 (3000)
Maximum flow, m^3/min (gpm)	0.95 (250)	1.8 (475)
Rapid mix retention time, seconds	30	30
Flocculation retention time, minutes	10	10
Rapid mix chamber volume, m^3 (gal)	0.48 (125)	0.96 (250)
Flocculation chamber volume, m^3 (gal)	0.5 (2500)	19.0 (5000)
Clarifier overflow rate, m^3/day-m^2 (gpd/ft^2)	204 (500)	204 (500)
Clarifier diameter, m (ft)	9.14 (30)	12.8 (42)
No. of clarifiers	1	1

APPENDIX D: ANALYTICAL METHODS--DEPOSIT ANALYSIS

THE DETERMINATION OF CALCIUM AND MAGNESIUM

(METHODS FOR BOILER SCALE ANALYSES)

PRINCIPLE

A solution of the deposit (from the boiler probe) is aspirated into a flame where metal ions are converted into an atomic vapor which is capable of absorbing radiation. The energy removed by those atoms in the ground state is a measure of concentration of the metal of interest.

SCOPE

The procedures are suited to hydrochloric acid solutions of the deposits. The methods have a sensitivity of 0.2 ppm for either metal and exhibit a precision in the order of ± 0.1 ppm over the 0-5 ppm range. No direct interferences are known; however, best accuracy can be obtained by preparing standards similar in composition to the samples.

REAGENTS AND SUPPLIES

1. Stock solution of calcium (1000 ppm) Fisher Chemical Index SO-C-191.

2. Stock solution of magnesium (1000 ppm) Fisher Chemical Index SO-M-51.

3. Lanthanum Oxide (Matheson Coleman and Bell) Catalogue number LX45-8229.

   Dissolve 58.6 gms of La_2O_3 in 400 ml of 50% HCl and dilute to one liter with double distilled water.

4. Hydrochloric Acid, concentrated.

5. Double distilled water.

6. Acetylene, commercial grade, cylinder.

EQUIPMENT

1. Atomic Absorption Spectrophotomer. (Perkin-Elmer 403 is suitable) equipped with Boling or suitable burner.

2. Recorder or other readout accessory.

3. Hollow cathode tube; combination Ca and Mg available from Perkin-Elmer.

PROCEDURE

1. General Procedure

a. Instrumentation

The analyst should familiarize himself with the manufacturer's operating instructions for the particular instrument involved. In general, after choosing the correct hollow cathode lamp, it should be allowed a 15-minute warm-up period. During this time, selection of the proper wavelength is made; slit adjustments are carried out, and the hollow cathode tube current is adjusted. Follow the manufacturer's recommendations for lighting and regulating the flame so that stable conditions result. Standards may now be run and calibration curve can be constructed, or for those instruments which read directly in connection (P-E-403), set the curve corrector to read out the proper concentrations on the digital readout.

b. Preparation of Standard Solutions and Calibration

Working from the stock solutions of the appropriate metal, standards are prepared to cover the working areas of interest. For best results calibration standards should be prepared fresh each time a run is made. Beginning with the blank and after stable instrumental conditions have been obtained, aspirate each of the standards from low to high and record the data. This can be done by means of a recorder, or if the equipment is so equipped, by means of the readout device.

2. Determination of Calcium

a. Instrumental Parameters

Aspirate the samples using direct readout, or compare the generated signals to a previously prepared calibration curve and report results as ppm Ca using proper factors if the sample was diluted.

3. Determination of Magnesium

a. Instrumental Parameters

(1) Hollow cathode tube	Calcium-magnesium
(2) Wavelength	2852A (UV)
(3) Burner	Boiling, rotate to 55° setting
(4) Oxidant	Air: Flow Meter Setting = 55
(5) Fuel	Acetylene: Flow Meter Setting = 35

(6) Flame conditions	Reducing
(7) Slit Setting	4
(8) Readout Time	10 seconds

b. Optimum concentration range

(1) 0-15 ppm (use scale setting 0.5A)
(2) 0-5 ppm (use scale setting 0.25A)

c. Preparation of Standards

Prepare dilutions of the stock magnesium solution for the concentration range desired. Pipet 20 ml of each standard and 5 ml of lanthanum solution into a plastic vial and mix well. Establish the calibration curve. It has been found convenient to preset the highest working standard at approximately 75% of full-scale deflection for either range.

d. Sample Analysis

Since magnesium is run on the sample that has been used to determine calcium, directions are the same as previously described.

DETERMINATION OF TOTAL AND SOLUBLE IRON

OPTIMUM CONCENTRATION RANGE:

0.1 - 5.0 mg/l using the 2483A line. For iron concentration below 0.1 mg/l use the extraction procedure. For iron concentration above 5 mg/l dilute samples with deionized water.

APPARATUS REQUIRED:

Water bath
Perkin-Elmer 303 or 403 Atomic Absorption Spectrophotometer

CHEMICALS REQUIRED:

1. Concentrated Hydrochloric Acid, Reagent Grade

2. 1000 ppm Fe standard. Dissolve 1.000 g reagent grade iron wire in 50 ml (1+1) HNO_3. Dilute to 1 liter with deionized water. One ml equals 1 mg Fe.

3. 10 ppm Fe standard. Pipet 10.0 ml of the 1000 ppm Fe standard into a 1 liter volumetric flask. Dilute to volume with deionized water.

4. 0.1, 0.5, 1.0, 2.0 and 5.0 ppm Fe standards. Pipet 1.0, 5.0, 10.0, 20.0 and 50 ml of the 10 ppm Fe standard into 100 ml volumetric flasks. Dilute to 100 ml with the deionized water. These solutions are 0.1, 0.5, 1.0, 2.0 and 5.0 ppm Fe standard, respectively.

PROCEDURE FOR TEST:

a. Total iron - shake sample and proceed as in (c).

b. Soluble Iron - filter sample through a 0.45 micron membrane filter and proceed as in (c).

c. To each 100 ml of sample in the polyethylene bottle add 1 ml of concentrated HCl. Heat the fixed sample in water bath at 90-95°C for four hours. Allow to cool to room temperature.

   Set up Atomic Absorption Spectrophotometer according to the following parameters:

1. Iron hollow cathode lamp
2. Wavelength - 2483A (248-UV)
3. Slit - 4 (7A)
4. Type burner - Boling (3-slot)
5. Fuel - acetylene
6. Oxidant - air

CALCULATION OF RESULTS:

Set up 0.1, 0.5, 1.0, 2.0 and 5.0 ppm Fe standards to readout 0.1, 5.0, 1.0, 2.0 and 5.0 on the digital readout. Aspirate the fixed samples directly from the polyethylene bottles and report as ppm iron (Fe).

ORTHOPHOSPHATE

TOTAL PHOSPHATE

APPARATUS REQUIRED:

Filter photometer
Erlenmeyer flask, 125 ml
Pipettes, 1 ml
Pipettes, 2.5 ml
Pipettes, 5 ml
Pipettes, 10 ml
Beakers, 50 ml

CHEMICALS REQUIRED:

Hydrochloric acid, concentrated, C.P.
Molybdate reagent
Phenolphthalein indicator
Stannous chloride, crystals
Standard phosphate solution, 45 ppm PO_4
Sodium hydroxide, 7N
Sulfuric acid, 50%

PROCEDURE FOR TESTS:

A fresh concentrated stock solution of stannous chloride should be prepared once each month. For this purpose add 12 gms stannous chloride crystals to 88 gms of C.P. concentrated hydrochloric acid. Store in an amber bottle away from light. Keep container tightly closed.

The dilute stannous chloride reagent used in this test must be prepared fresh daily. The dilute reagent consists of 1.0 ml of concentrated stannous chloride diluted to a total volume of 40 ml with distilled water.

This procedure employs a wavelength of 610 mu and a light path of 5 mm. Prepare calibration curves for the photometer using successive dilutions of the phosphate standard to adequately cover the range of phosphate in the samples to be tested. Two curves are required--one for orthophosphate and one for total phosphate. The dilutions of the standard should be treated in exactly the same manner as that shown below for analysis of the water samples.

Each time a determination is made the calibration curves should be checked to establish a correction factor. This procedure is necessary to insure that the results are accurate since reagent age and stability as well as temperature can affect the results. Each curve should be checked with phosphate-free water and also at a dilution of the phosphate standard that approximates the middle of the phosphate range covered by the curves. It is very important that the "check" samples are analyzed at the same time, under the same conditions and treated in the same manner as the actual water samples. Do not omit any of the steps as the conversion procedure, etc.

Phosphate must be determined on a filtered sample, using a filter paper such as Whatman No. 5. Discard the first 10-20 ml of filtrate since there is a slight adsorption of phosphate by fresh filter paper.

TO DETERMINE ORTHOPHOSPHATE:

Prepare a "zero" reference blank by adding to a beaker; 5 ml of clear sample, 10 ml molybdate reagent and 2.5 ml distilled water. Use this solution to set the photometer at "zero" immediately prior to test.

To a second beaker add 5 ml clear sample, 10 ml molybdate reagent and 2.5 ml dilute stannous reagent. Allow to stand one (1) minute and then immediately obtain photometer dial reading.

TO DETERMINE TOTAL PHOSPHATE:

In order to determine total phosphate, it is necessary to convert all polyphosphate in the sample to orthophosphate. Place two 25-ml clear samples in separate 125-ml Erlenmeyer flasks. One sample is to be used as a blank and the other for analysis. To each flask add 2.5 ml 50% sulfuric acid. Boil both the blank and the sample vigorously for at least 30 minutes. Add distilled water periodically so that the volume does not fall below 5 ml. If the volume does fall below 5 ml, the sample must be discarded. If it is not convenient to observe the sample continuously during boiling, reflux condensers may be employed.

Cool the blank and the sample to room temperature. Add 3 drops phenolphthalein indicator to each flask and neutralize with 7N sodium hydroxide (approximately 5 ml will be required) until a faint permanent pink appears. Add 50% sulfuric acid, drop by drop, until the solutions turn colorless.

Since some heat may be generated during neutralization, recool and then adjust the volumes to exactly 25 ml with distilled water. A precipitate may form at this point but do not filter.

The total phosphate now can be determined. Measure 5 ml of the blank and 5 ml of the sample after shaking to be sure a representative amount of any precipitate is included. Proceed in exactly the same manner as shown for orthophosphate.

CALCULATION OF RESULTS:

The orthophosphate and total phosphate values in parts per million as PO_4 are obtained directly from their respective calibration curves. The polyphosphosphate concentration is obtained by subtracting the value for orthophosphate from the value for total phosphate.

DETERMINATION OF SILICA

0.0-3.0 ppm

APPARATUS REQUIRED:

Filter photometer
Pipettes, 5 ml
Beakers, 100 ml

CHEMICALS REQUIRED:

Ammonium molybdate reagent (low range)
Oxalic acid, 3%
Amino-Naphthol-Sulfonic acid
Silica standard, 50 ppm SiO_2

PROCEDURE FOR TEST:

This procedure employs a wavelength of 690 mu and a cell with a light path of 40 mm. Prepare a calibration curve for the photometer using successive dilutions of the silica standard to adequately cover the anticipated range of silica in the samples to be tested. The dilutions of the standard should be treated in exactly the same manner as that shown below for analysis of the water samples.

Each time a determination is made the calibration curve should be checked to establish a correction factor. This procedure is necessary to insure that the results are accurate since the reagent age and stability as well as temperature can affect the results. The curve should be checked with silica-free water and also at a dilution of the silica standard that approximates the middle of the silica range covered by the curve. All reagents as well as the "check" samples and the actual sample to be analyzed must be at the same temperature.

The amino-naphthol-sulfonic acid reagent used in this test is not stable and should be prepared once each week. Dissolve 1.0 g of 1-amino, 2-naphthol, 4-sulfonic acid in 4.5 ml of 1N sodium hydroxide. Add with 60 g sodium bisulfite and 2 g sodium sulfite to 900 ml distilled water. Dilute to 1.0 liter with distilled water.

Prepare a "zero" reference blank. To a beaker, add 50 ml of the clear sample, 5 ml oxalic acid, 5 ml sulfonic acid and 5 ml distilled water. Use this blank to set the photometer at "zero" immediately prior to the test of a sample.

To a second beaker, add 50 ml samples, and 5 ml ammonium molybdate reagent. Allow to stand approximately 5 minutes. Add 5 ml oxalic acid reagent. Wait approximately one minute and then add 5 ml sulfonic acid reagent. Allow to stand exactly two minutes and immediately obtain dial reading.

CALCULATION OF RESULTS:

The silica concentration in parts per million as SiO_2 is obtained by reference to the prepared silica calibration curve.

DETERMINATION OF SILICA (SiO_2)

3-50 ppm

APPARATUS REQUIRED:

Perkin-Elmer 403

REAGENTS REQUIRED:

1. 1000 ppm SiO_2 standard - Obtain from Betz Lab Stock Division.
2. 150 ppm SiO_2 standard - Dilute 150 ml of the 1000 ppm SiO_2 standard to 1 liter with deionized water.
3. 50-25-5 ppm SiO_2 standards - Pipet 50.0, 25.0 and 5.0 ml of the 1000 ppm standard into 1-liter volumetric flasks and dilute to volume with deionized water.
4. 3 ppm standard - Pipet 20 ml of the 150 ppm SiO_2 standard into a 1-liter volumetric glask and dilute to volume with deionized water.

PROCEDURE:

Set up the Atomic Absorption Spectrophotometer according to the following parameters:

1. Silicon hollow cathode tube.
2. Wavelength - 2516A (252-UV)
3. Slit - 4 (7A)
4. Type burner - nitrous oxide
5. Fuel - acetylene
6. Oxidant - nitrous oxide

Set the mode on absorbance and with the 150 ppm SiO_2 standard, adjust burner position for maximum absorbance.

CALCULATION OF RESULTS:

Then switch to concentration mode and set up the 50, 25, 10 and 3 ppm calibration standards to read 50, 25, 10 and 3 on the digital readout. Aspirate settled samples directly from the polyethylene sampling bottles and read ppm SiO_2 from the digital readout.

NOTE: Reject SiO_2 values below 3.0 ppm. They must be analyzed colorimetrically.

A) Analytical results on deposit analysis are reported as follows:

Calcium as Ca = ppm

Phosphate as PO_4 = ppm

Magnesium as Mg = ppm

Silica as SiO_2 = ppm

Total Iron as Fe = ppm

Insolubles = mg

sample size = 0.25 l

heat transfer area = 0.017 m^2

B) Conversion of deposit weight (from ppm to g/m^2)

1. Calcium (Ca)

   ppm Ca x (1 g/l)/1000 ppm x 0.25 l x 1/0.017 m^2 = g/m^2 Ca

2. Phosphate ($PO_4 \longrightarrow P_2O_5$).

   ppm PO_4 x 142 (P_2O_5)/190 ($2PO_4$) x (1 g/l)/1000 ppm x 0.25 l x 0.017 m^2 = g/m^2 P_2O_5.

3. Magnesium ($Mg \longrightarrow MgO$)

   ppm Mg x 40 (MgO)/24 (Mg) x (1 g/l)/1000 ppm x 0.25 l x 0.017 m^2 = g/m^2 MgO

4. Silica (SiO_2)

   ppm SiO_2 x (1 g/l)/1000 ppm x 0.25 l x 0.017 m^2 = g/m^2 SiO_2

5. Total Iron (Fe ⟶ Fe_2O_3)

ppm Fe x 160 (Fe_2O_3)/112 (2 Fe) x (1 g/l)/1000 ppm x 0.25 l x 0.017 m^2 = g/m^2 Fe_2O_3

6. Insolubles

mg x 1 g/1000 mg x 1/0.017 m^2 = g/m^2 insolubles.

APPENDIX E: CALCULATION OF CORROSION TEST COUPON PENETRATION RATE

CORROSION TEST COUPON PENETRATION RATE CALCULATION

In calculating the penetration per year from the test corrosion coupons the following formula is applied:

$$\text{Avg. P (mils per year)} = \frac{\text{Weight Loss} \times 0.061}{\text{Sp. Gravity} \times A \times \text{time} \times 1/365}$$

Avg. P = Average penetration (mils per year).

Weight Loss = Loss of weight of specimen in milligrams.

0.061 = Cubic inches per cubic centimeter.

Sp. Gravity = Specific Gravity of material used.

A = Area in square inches (normally for our specimen 3 sq. in.).

Time = Time of exposure in days.

1/365 = Reciprocal of days in year.

Employing the above formula, reduce all constant values to one single factor so that average P (mils per year) will equal weight loss in milligrams divided by the number of days exposed times a factor.

$$\text{Avg. P (mils per year)} = \frac{\text{weight loss}}{\text{days exposed}} \times f$$

Listed below are the various metals and their specific gravities that Betz Laboratory presently employs with the proper factor.

Metal	Sp. Gravity	f (Factor)
Admiralty	8.52	0.871
Low Carbon Steel	7.84	0.946
Copper	8.95	0.829
Aluminum	2.76	2.69
Cast Iron	7.0	1.06
Brass	8.49	0.874